PB81-173882

Land Disposal: Hazardous Waste Proceedings of the Seventh Annual Research Symposium Held at Philadelphia, Pennsylvania on March 16-18, 1981

Southwest Research Inst.
San Antonio, TX

Prepared for

Municipal Environmental Research Lab.
Cincinnati, OH

Mar 81

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/9-81-002b	2.	3. RECIPIENT'S ACCESSION NO. PB81 173882
4. TITLE AND SUBTITLE Land Disposal: Hazardous Waste Proceedings of the Seventh Annual Research Symposium		5. REPORT DATE March 1981 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Edited by David Shultz Coordinated by David Black		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Southwest Research Institute P. O. Drawer 28510 San Antonio, TX 78284		10. PROGRAM ELEMENT NO. BRD1A DU109 11. CONTRACT/GRANT NO. 68-03-2962
12. SPONSORING AGENCY NAME AND ADDRESS Municipal Environmental Research Laboratory--Cin.,OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268		13. TYPE OF REPORT AND PERIOD COVERED Final - 9/20-3/81 14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES

Project Officer Robert E. Landreth, 684-7871

16. ABSTRACT

The Seventh Annual SHWRD Research Symposium on land disposal of municipal solid waste and industrial solid waste and resource recovery of municipal solid waste was held in Philadelphia, Pennsylvania, on March 16, 17, and 18, 1981. The purposs of the symposium were (1) to provide a forum for a state-of-the-art review and discussion of on-going and recently completed research projects dealing with the management of solid and industrial wastes; (2) to bring together people concerned with municipal solid waste management who can benefit from an exchange of ideas and information; and (3) to provide an arena for the peer review of SHWRD's overall research program. These proceedings are a compilation of papers presented by the symposium speakers. The technical areas covered in the Land Disposal: Municipal Solid Waste are gas and leachate production, treatment and control technologies and economics. The areas covered in Land Disposal: Hazardous Wastes are hazardous waste characterization, transport and fate of pollutants, hazardous waste containment, land treatment of hazardous wastes, hazardous waste treatment, uncontrolled sites/remedial action, and economics. Municipal Solid Waste: Resource Recovery include the areas of equipment and processing, recovery and use of materials, environmental aspects and economics/impediments and special studies.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Leaching Collection, Hazardous Materials, Disposal, Treatment, Soils, Groundwater Pollution, Waste Treatment, Methane, Gases, Linings	Solid Waste Management Sanitary Landfills Hazardous Waste Leachate	13B

18. DISTRIBUTION STATEMENT Release to public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

☆ U.S. GOVERNMENT PRINTING OFFICE: 1981-757-064/0244

United States
Environmental Protection
Agency

Municipal Environmental Research
Laboratory
Cincinnati OH 45268

EPA-600/9-81-002b
March 1981

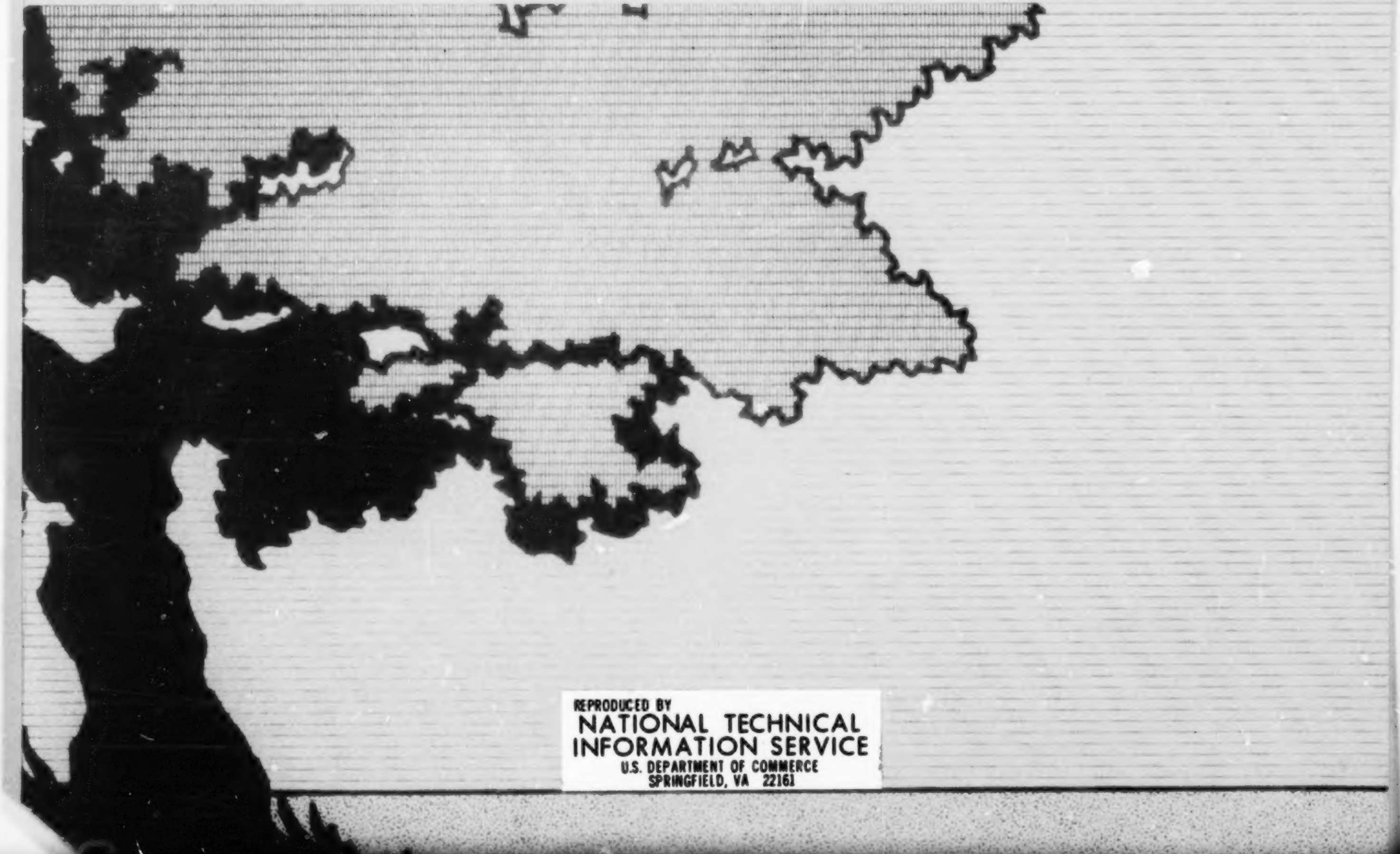
PB81-173882

Research and Development

EPA

Land Disposal: Hazardous Waste

Proceedings of the Seventh Annual Research Symposium



REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/9-81-002b
March 1981

LAND DISPOSAL: HAZARDOUS WASTE

Proceedings of the Seventh Annual Research Symposium
at Philadelphia, Pennsylvania, March 16-18, 1981
Sponsored by the U.S. EPA, Office of Research & Development
Municipal Environmental Research Laboratory
Solid and Hazardous Waste Research Division

Edited by: David W. Shultz

Coordinated by: David Black

Southwest Research Institute
San Antonio, Texas 78284

Contract No. 68-03-2962

Project Officer

Robert E. Landreth
Solid and Hazardous Waste Research Division
Municipal Environmental Research Laboratory
Cincinnati, Ohio 45268

MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

i.a

DISCLAIMER

These Proceedings have been reviewed by the U.S. Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

The Environmental Protection Agency was created because of increasing public and governmental concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of the environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is the first necessary step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and the solid and hazardous waste pollutant discharges from municipal and community sources; to preserve and treat public drinking water supplies; and to minimize the adverse economic, social, health and aesthetic effects of pollution. This publication is one of the products of that research--a vital communications link between the researcher and the user community.

These Proceedings present the results of completed and ongoing research projects concerning the land disposal of hazardous waste.

Francis T. Mayo
Director
Municipal Environmental
Research Laboratory

PREFACE

These Proceedings are intended to disseminate up-to-date information on extramural research projects concerning the land disposal of hazardous wastes. These projects are funded by the Solid and Hazardous Waste Research Division (SHWRD) of the U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory in Cincinnati, Ohio.

The papers in these Proceedings are arranged as they were presented at the symposium and have been printed basically as received from the authors. They do not necessarily reflect the policies and opinions of the U.S. Environmental Protection Agency. Hopefully, these proceedings will prove useful and beneficial to the scientific community as a current reference on the land disposal of hazardous wastes.

ABSTRACT

The Seventh Annual SHWRD Research Symposium on land disposal of municipal solid waste, hazardous waste, and resource recovery of municipal solid waste was held in Philadelphia, Pennsylvania, on March 16, 17, and 18, 1981. The purposes of the symposium were (1) to provide a forum for a state-of-the-art review and discussion of ongoing and recently completed research projects dealing with the management of solid and hazardous wastes; (2) to bring together people concerned with municipal solid waste management who can benefit from an exchange of ideas and information; and (3) to provide an arena for the peer review of SHWRD's overall research program. These Proceedings are a compilation of papers presented by the symposium speakers.

The symposium proceedings are being published as three separate documents. In this document, Land Disposal: Hazardous Waste, seven technical areas are covered. They are as follows:

(1) Hazardous waste characterization
(2) Transport and fate of pollutants
(3) Hazardous waste containment
(4) Land treatment of hazardous waste
(5) Hazardous waste treatment
(6) Uncontrolled sites/remedial action
(7) Economics

TABLE OF CONTENTS

SESSION C - HAZARDOUS WASTE MANAGEMENT

Page

Overview: Current Research on Land Disposal of Hazardous Wastes ix

Session C-1. Hazardous Waste Characterization

Improved Techniques for Flow of Liquids through Hazardous Waste Landfills 1

Development of a Solid Waste Leaching Procedure and Manual 9

Session C-2. Transport and Fate of Pollutants

Behavior of Cd, Ni, and Zn in Single and Mixed Combinations in Landfill Leachates 18

Aqueous Chemistry and Adsorption of Hexachlorocyclopentadiene by Earth Materials 29

Methods of Soil Hydraulic Conductivity Determination and Interpretation 43

Evaluation of Molecular Modelling Techniques to Estimate the Mobility of Organic Chemicals in Soils: II. Water Solubility and the Molecular Fragment Mobility Coefficient 58

Prediction of Leachate Plume Migration 71

Mechanisms and Models for Predicting the Desorption of Volatile Chemicals from Wastewater 85

Session C-3. Hazardous Waste Containment

Management of Hazardous Waste by Unique Encapsulation Processes . . . 91

Estimation of Pollution Potential of Industrial Waste from Small-Scale-Column Leaching Studies 103

Organic Leachate Effects on the Permeability of Clay Liners 119

Membrane Liner Systems for Hazardous Waste Landfills 131

Durability of Liner Materials for Hazardous Waste Disposal Facilities 140

Table of Contents (cont'd)

Page

Installation Practices for Liners 157

Session C-4. Land Treatment of Hazardous Wastes

Identification of Hazardous Waste for Waste Treatment Research. . . . 168

Statistical Analysis of Trace Metal Concentrations in Soils at Selected Land Treatment Sites 178

Factors Influencing the Biodegradation of API Separator Sludges Applied to Soils 188

Review and Preliminary Studies of Industrial Land Treatment Practices 200

Assessment of Hydrocarbon Emissions from Land Treatment of Oily Sludges 213

The Development of Laboratory and Field Studies to Determine the Fate of Mutagenic Compounds from Land Applied Hazardous Waste . 224

Closure Techniques at a Petroleum Land Treatment Site 240

Land Treating Tannery Sludges Initiation of a Five Year Investigation 246

Session C-5. Hazardous Waste Treatment

Inorganic Hazardous Waste Treatment. II 250

Emerging Technologies for the Destruction of Hazardous Waste Ultraviolet/Ozone Destruction 265

Evaluation of Catalyzed Wet Oxidation for Treating Hazardous Wastes 272

Registration Requirements for Pesticide Labeling - Land Disposal . . 277

Preliminary Studies Evaluating Composting as a Means for Pesticide Disposal 283

Session C-6. Uncontrolled Sites/Remedial Action

Top Sealing to Minimize Leachate Generation - Status Report 291

Investigation of the LiPari Landfill Using Geophysical Techniques . . 298

Remedial Actions at Uncontrolled Hazardous Waste Sites 312

Barrel and Drum Reconditioning Industry Status Profile 320

Table of Contents (cont'd)

Page

Bench Scale Assessment of Concentration Technologies for Hazardous Aqueous Waste Treatment 341

Application of Remote Sensing Techniques to Evaluate Subsurface Contamination and Buried Drums 352

Session C-7. Economics

Conceptual Cost Analysis of Remedial Actions at Uncontrolled Sites 366

Regulating Illegal Dumping of Hazardous Wastes 387

CURRENT RESEARCH ON LAND DISPOSAL OF HAZARDOUS WASTES

Norbert B. Schomaker
John V. Klingshirn
Michele A. Gualtieri
U.S. Environmental Protection Agency
26 West St. Clair Street
Cincinnati, Ohio 45268

ABSTRACT

The Solid and Hazardous Waste Research Division (SHWRD), Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, in Cincinnati, Ohio, has responsibility for research in solid and hazardous waste management in the area of waste disposal to the land. To fulfill this responsibility, the SHWRD is developing concepts and technology for new and improved systems of solid and hazardous waste land disposal; is documenting the environmental effects of various waste disposal practices; and is collecting data necessary to support implementation of disposal guidelines mandated by the "Resource Conservation and Recovery Act of 1976 (RCRA)" PL 94-580. This paper will present an overview of the land disposal aspects of the SHWRD Hazardous Waste Program Plan and will report the current status of work in the following categorical area:

A. LANDFILL DESIGN CRITERIA
    1. Waste Leaching and Analysis
    2. Pollution Migration
    3. Pollutant Control
    4. Waste Modification
B. LANDFILL ALTERNATIVES
    1. Land Treatment
    2. Surface Impoundments
C. UNCONTROLLED SITES/REMEDIAL ACTION
D. ECONOMIC ASSESSMENT

INTRODUCTION

The waste residual disposal research strategy, encompassing state-of-the-art documents, laboratory analysis, bench and pilot studies, and full-scale field verification studies is at various stages of implementation. Over the next 5 years the research will be reported as criteria and guidance documents for user communities. The waste disposal research program is currently developing and compiling a data base for use in the development of guidelines and standards for waste residual disposal to the land as mandated by the "Resource Conservation and Recovery Act of 1976" (RCRA). Permit Writer's Guidance Manuals which provide guidance for conducting the review and evaluation of permit applications are currently being prepared. Technical Resource Documents in support of the Guidance Manuals are also being prepared in specific areas to provide current technologies and methods for evaluating the performance of the applicant's design. The information and guidance presented in these manuals will constitute a suggested approach for review and evaluation based on best engineering judgements.

The current waste residual disposal research program has been divided into four general areas: (a) Design Considerations for Current Landfill Disposal

Techniques; (b) Alternatives to Current Landfill Disposal Techniques; (c) Remedial Action for Minimizing Pollutants from Unacceptable or Inoperative Sites; and (d) Economic Assessment of Hazardous Waste Disposal Practices and Alternatives.

The waste residual research program has been discussed in the previous six symposia. These symposia describe both the land disposal of municipal and hazardous waste. The most recent symposium was on Research on Land Disposal of Hazardous Wastes: "Proceedings of the Sixth Annual Research Symposium: March 17-20, 1980, Chicago, Illinois, EPA-600/9-80-010.

LANDFILL DESIGN CRITERIA

Waste Leaching and Analysis

The overall objective of this research activity is to provide information on the toxicity and compatibility of hazardous wastes and their generated leachates.

Analysis of the contaminants within a waste leachate sample is difficult due to interfering agents. Existing USEPA procedures have been developed on an as-needed basis as part of the SHWRD projects. However most of this work is specific to the wastes being studied and separate efforts were required to insure that more general procedures/equipment would be developed.

One effort (1) in the waste leaching and analytical techniques area is directed towards analytical methods for applicability in leaching analysis. Physical and chemical methods were evaluated for their applicability in analysis of contaminated industrial leachate streams. The results of this completed effort will be published in a report entitled "Analytical Methods Evaluation for Applicability in Leaching Analysis".

A second effort (1) has developed and validated recommended test procedures for toxicity of leachates and extracts of wastes. This completed effort has been published in a report entitled "Toxicity of Leachates" EPA-600/2-80-057, March 1980.

This area of research activity has recently been transferred to another USEPA research group with the "Environmental Monitoring and Support Laboratory" at Las Vegas, Nevada.

Standard Sampling Techniques

Standard Sampling procedures, including collection, preservation, and storage of samples, do not exist for solid and semi-solid wastes. Existing procedures for sampling liquid effluents and soils must be adapted to a variety of circumstances. Experience with sampling procedures has been accumulated as part of several on-going SHWRD projects.

One effort (2) in the sampling technique area was an activity to standardize methods for sampling and analysis of hazardous wastes. The findings of this completed effort have been published in a report entitled "Samplers and Sampling Procedures for Hazardous Waste Streams" EPA-600/2-80-018, January 1980. This effort has been expanded to include development of a list of reactive wastes and test methods for those wastes thought to cause serious problems.

This expanded effort (2) has produced a method for determining the compatibility of binary combinations of hazardous waste. This method consists of a step-by-step analysis procedure after which a compatibility chart can be read. This method, chart included, has been published in the report entitled "A Method for Determining the Compatibility of Hazardous Wastes" EPA-600/2-80-076, April 1980.

A second effort (2) with objectives similar to the previous effort has developed a protocol for field testing of reactive wastes that may cause serious problems.

A third effort (1) has determined which sampling and preservation techniques should be acceptable as standards for groundwater sampling. Six landfill monitoring wells have been studied using four different pumping techniques and thirteen different sample preservation procedures. The results of this completed effort will be published in a report entitled "Monitoring Well Sampling and Preservation Techniques".

---

(1) Paranthesis numbers refer to the project officers listed immediately following this paper who can be contacted for additional information.

This area of research activity has recently been transferred to another USEPA research group with the "Environmental Monitoring and Support Laboratory" at Las Vegas, Nevada.

Co-Disposal Generated Leachates

The overall objective of the co-disposal activity is to assess the impact of the disposal of industrial waste materials with municipal solid waste. Because the environmental effects from landfilling result from not only the soluble and slowly soluble materials placed in the landfill but also the products of chemical and microbiological transformation, these transformations should be a consideration in management of a landfill to the extent that they can be predicted or influenced by disposal operations.

One ongoing effort (5) involves a study of the factors influencing (a) the rate of decomposition of solid waste in a sanitary landfill, (b) the quantity and quality of gas and leachate produced during decomposition, and (c) the effect of admixing industrial sludges and sewage sludge with municipal refuse. A combination of municipal solid waste and various solid and semi-solid industrial wastes was added to several field lysimeters. The industrial wastes investigated were: petroleum sludge, battery production waste, electroplating waste, inorganic pigment sludge, chlorine production brine sludge, and a solvent-based paint sludge. Also, municipal digested primary sewage sludge dewatered to approximately 20 percent solids was utilized at three different ratios. The results of this effort have been reported in a paper entitled Co-Disposal of Industrial and Municipal Wastes in a Landfill: "Proceedings of the Fourth Annual Research Symposium" EPA-600/9-78-016, August 1978, pp. 129-151. The updated results of this effort have been published in a paper entitled Leachate From Municipal and Industrial Waste Simulators: "Proceedings of the Sixth Annual Research Symposium" EPA-600/2-80-010, March 1980, pp. 203-222.

Pollutant Migration

The overall objective of this research activity is to develop procedures for using soil as a predictable attentuation medium for pollutants. Not all pollutants are attenuated by soil, and in some cases, the process is one of delay so that the pollutant is diluted in other parts of the environment. Consequently, a significant number of the research projects funded by SHWRD are focused on understanding the process and predicting the extent of migration of contaminants (chiefly heavy metals) from waste disposal sites. Both laboratory and field verification studies at selected sites are being performed to assess the potential for groundwater contamination. The studies will provide the information required to (a) select land disposal sites that will naturally limit release of pollutants to the air and water and (b) make rational assessments of the need for the cost-benefit aspects of leachate and gas control technology. Progress has been made using soil and waste characteristics to predict movement of pollutants in soil, but the results are not sufficiently comprehensive nor have they been field tested significantly to qualify as a basis for disposal regulations that will be challenged most assuredly in legal proceedings. Work is in progress on empiricial predictive techniques using samples of wastes and soils from locations of specific interest. This approach appears to be the most promising in order to integrate the effect of waste and soil characteristics on pollutant retention processes. The precision and accuracy that will be achieved by this method remains to be determined.

One on-going effort (4) is the development of a Guidance Document addressing: (a) to what degree leachate concentrations will be reduced by mixing with groundwater in the vicinity of waste disposal sites in a variety of hydrogeologic situations (b) the direction of movement and shape of leachate plumes, and (c) the types of models that are appropriate for predicting movement of solutes in groundwater at sites with specific hydrogeologic characteristics, assuming that solutes do not interact with aquifer materials.

A second effort (4) examined the extent to which hazardous substances from specific industrial and flue gas cleaning (FGC) wastes would migrate into groundwater at disposal sites. Procedures for conducting such examinations have been developed. Leachate from a municipal solid waste landfill was used to extract the following industrial wastes: electroplating, inorganic pigment, water based paint, Hg cell chlorine production and Ni-Cd battery. A sequential batch leaching/ soil adsorption procedure was developed which provides information comparable to that obtained from soil column studies, but in a much shorter time. The results of this completed effort will be published in a report entitled "Migration of Hazardous Substance Through Soil".

A third effort (4) was the development and testing of a large scale hydrogeologic simulation model for predicting the movement of nonconservative solutes in saturated and unsaturated soils. The two-dimensional model used successfully to study a chromium contamination problem has been developed into a three-dimensional model. The results of this completed effort will be published in a report entitled "Hydrologic Simulation on Solid Waste Disposal Sites".

A fourth effort (4) is the on-going development of user oriented models for predicting movement in soil as a basis for improving selection of sites for disposing of solid and hazardous wastes. Average movement rates of Cd, Ni, and Zn from industrial waste leachates in soils will be measured and the Lapidus Amundson solute movement model will be used to predict long term steady state movement rates for each set of experimental conditions. Long term movement rates will then be correlated with soil and leachate properties to develop regression equations forming a basis for a simplified predictive tool.

A fifth effort (4) studied vertical and horizontal contaminant migration of Zn, Cd, Cu and Pb at three secondary zinc smelting plants and one organic chemical manufacturing plant. Migration patterns were defined using soil coring and monitoring well techniques. Soil coring was determined to be an investigative tool, but not suitable by itself for routine monitoring of waste disposal activities. The results of this study are currently being published in a report entitled "Field Verification of Toxic Wastes Retention by Soils at Disposal Sites."

A sixth effort (4) was the determination of the attenuation mechanisms and capacity of selected clay minerals and soils for hexachlorocyclopropentadial (HCCPD) and "hex" wastes. Also, effects of caustic-soda brine on the attenuation and solubility of HCCPD and the development of a chemical model to predict HCCPD migration through soil were pursued. Mobility of HCCPD in soils was independently assessed by use of soil thin-layer chromatography and column leaching techniques. The results of this completed effort will be published in a report entitled "Assessment of Soil, Clay and Caustic Soda Effects on Land Disposal of Hydrocarbon Wastes (HCCPD)".

A seventh effort (2) studied organic contaminant attenuation by selected clay minerals and coal chars. Initial work was with Polychlorinated biphenyls (PCBs); subsequent efforts were with Hexachlorobenzene (HCB) and Polybrominated biphenyls (PBBs). The mobility of Arochlors 1242 and 1254, and a used capacitor fluid were measured by the soil thin-layer chromatography technique and additional batch adsorption studies were conducted. PCBs were found to be strongly adsorbed by soil materials. The adsorption capacity and the mobility of PCBs were positively correlated to the organic carbon content and surface area of the respective soil materials. The results of this effort will be published in a report entitled "Attenuation of Polybrominated Biphenyls and Hexachlorobenzene by Earth Materials".

An eight effort (3) currently underway, aims to develop a guidance manual identifying wastes that increase the permeability of soils at a disposal site. Test procedures for predicting whether a specific waste and soil will react to increase soil permeability will be developed.

A ninth effort (4) is currently underway to determine how accurately the EPA Gas Movement Model predicts the maximum distance that methane gas will move through soils adjacent to landfills and how accurately this model will predict the relative effectiveness of control systems (e.g., trenches, wells, barriers) for minimizing methane gas movement.

The extent of methane movement will be measured at three selected landfills. With data from each landfill, the model will be used to predict the maximum extent of methane movement. The measured and predicted methane movements will be compared, reasons for any differences analyzed, and the accuracy and effort of use for the model determined.

A tenth effort (5) has resulted in establishment of guidelines for design of gas migration control devices for sanitary landfills. The migration control devices studied included trenches venting under natural convection, trenches with exhaust pumping, trenches with recharge pumping, barriers, hybrid systems consisting of a barrier with a pumped (exhaust or recharge) or unpumped trench on the landfill site, and pumped (exhaust or recharge) pipe vents. Computer codes developed under a previous study (c.f. Moore and Alzaydi, 1977: and Moore and Rai, 1977) were modified to incorporate pressure flow as well as diffusional flow. The results of this completed effort will be published in a report entitled "Gas Control Design Criteria".

An eleventh effort (4) has evaluated the conditions that would control the movement of hexachlorobenzene (HCB) out of landfills and other disposal/storage facilities into the surrounding atmosphere. The volatilization fluxes of hexachlorobenzene from industrial wastes (hex waste) were determined using coverings of soil, water and polyethylene film in a simulated landfill under controlled laboratory conditions. The results of this effort have been published in a report entitled "Land Disposal of Hexachlorobenzene Wastes - Controlling Vapor Movement in Soils," EPA-600/2-80-119, August 1980.

Pollutant Control

The overall objective of this research activity is to reduce the impact of pollution from waste disposal sites by technology that minimizes, contains, or eliminates pollutant release and leaching from waste residuals disposed to the land. The pollutant control studies are determining the ability of in-situ soils and natural soil processes to attenuate leachate contaminants as the leachate migrates through the soil from landfill sites. The studies are also determining how various synthetic and admixed materials may be utilized as liners to contain and prevent leachates from migrating from landfill sites.

Natural Soil Processes

The treatment by natural soil processes of pollutants from hazardous waste and municipal refuse disposal sites is being performed in the controlled lab studies previously discussed in the section on pollutant transport.

Liners/Membrane/Admixtures

The liner/membrane/admixture technology (3) is currently being studied to evaluate suitability for eliminating or reducing leachate from landfill sites of municipal or industrial hazardous wastes. The test program will evaluate in a landfill environment, the chemical resistance and durability of the liner materials over 12- and 36-month exposure periods to leachates derived from industrial waste, sulfur oxides (SO_x) wastes, and municipal solid wastes. Acidic, basic, and neutral solutions will be utilized to generate industrial waste leachates.

The liner materials being investigated under the hazardous waste program include five admixed materials and eight polymeric membranes. Specimens of these materials have been exposed for more than 3 years to the following six classes of hazardous wastes which utilized ten specific types of wastes: strong acid; strong base; waste of saturated and unsaturated oils; lead waste from gasoline tanks; oil refinery tank bottom waste (aromatic oil); and pesticide waste. Preliminary exposure tests have been completed on the various liner materials in the various wastes in order to select combinations for long term exposures. The results of these tests along with a discussion of the overall hazardous waste liner material program are presented in a report entitled "Liner Materials Exposed to Hazardous and Toxic Sludges First Interim Report," EPA-600/2-77-091, June 1977.

A second effort (3) relates to the types of materials tested for use as liners for sites receiving sludges generated by the removal of SO_x from flue gases of coal-burning power plants. The volumes of SO_x sludges generated in any particular place will, typically, be much greater than those for other types of wastes, and therefore the disposal sites will be large. Consequently, methods of lining such disposal sites must have a low unit cost for materials as well as labor. The admixed materials consisted of the following: cement; lime; cement with lime; polymeric bentonite blend (M179); gray powder-quartec (UF); asphaltic concrete; TACSS 020; TACSS 025; TACSS C400; and TACSS ST. The prefabricated membranes liner materials consisted of the following: elasticized polyolefin; black neoprene - coated nylon; and black neoprene - reinforced fabric. The spray-on liner materials consisted of the following: polyvinyl acetate; natural rubber latex; natural latex; polyvinyl acetate; asphalt cement; and molten sulphur. For this effort, a total of 72 special test cells were constructed to perform 12 and 24 month exposure tests. An interim report has been published entitled "Flue Gas Cleaning Sludge Leachate/Liner Compatibility Investigated: Interim Report, "EPA-600/2-79-136, August 1979. A final report will be published entitled "Effect of Flue Gas Cleaning Sludges on Selected Liner Materials".

A third effort (3) is an on-going study to assess actual field procedures utilized in (a) preparing the support subbase soil structure for liners and (b) placing the various liner materials common to projects requiring positive control of fluid loss. A fourth on-going effort (3) is concerned with determining the soil requirements to act as bedding and protective covers for flexible membranes. Experiments will be conducted using a variety of flexible membranes, base, and subbase materials, thicknesses and densities so that a design manual, applicable to the majority of the country, can be developed which will provide a design engineer with the data necessary to determine the most economic soil requirements above and below a flexible membrane. The results of this effort to date have been compiled in an unpublished report entitled "Membrane Liner Systems for Hazardous Waste Landfills".

A fifth on-going effort (3) responds to the need for support of the guidelines and hazardous waste criteria mandated under RCRA. This project has been designed to provide the EPA with data to enable annual revisions to the landfill liner design manual now being prepared. Furthermore, it will provide assistance in permit application evaluation, assessment of performance and expert testimony.

A sixth on-going effort (3) relates to evaluating long term performance of liner systems. As liner technology advances and new materials and design continue to be developed, these developments will be made available to liner users and permit writers through incorporation of information into the technical resource document, "Lining of Waste Impoundment and Disposal Facilities".

A seventh effort (3), now on-going, is primarily concerned with the evaluation of specific technologies (chemical liners) for the disposal and recovery of sludges from the metal finishing industry.

An eighth effort (4), now completed, relates to a laboratory study of agricultural limestone and hydrous oxides of Fe to evaluate their use as landfill liner materials to minimize the migration of metal contaminants. The results of this effort are being published in a report entitled "Liners of Natural Porous Materials to Minimize Pollutant Migration".

Waste Modification (Chemical Stabilization)

Chemical stabilization is achieved by incorporating the solid and liquid phases of a waste into a relatively inert matrix which exhibits increased physical strength and protects the components of the waste from dissolution by rainfall or by soil water. If this slows the rate of release of pollutants from the waste sufficiently and no serious stresses are exerted on the environment around the disposal site, then the wastes have been rendered essentially harmless and restrictions on siting will be minimal.

The initial chemical fixation effort (3) which is on-going relates to the transformation of wastes into an insoluble form to minimize leaching. The test program consists of investigating ten industrial waste streams in both the raw and fixed states. The waste streams are treated with at least one of seven separate fixation processes and subject to leaching and physical testing. The lab and field studies have been completed. The results have been compiled and discussed in a report entitled "Pollutant Potential of Raw and Chemically Fixed Hazardous Industrial Wastes and Flue Gas Desulfurization Sludges-Interim Report," EPA-600/2-76-182, July 1976. The final results of these studies will be reported in three reports entitled "Small Column Leaching Tests on FGD Sludges", "Small Column Leaching Tests on Industrial Sludges", and "Large Column Leaching Tests on FGD Sludge".

A second on-going effort (3) relates to the co-disposal of chemically treated and untreated industrial wastes in a municipal refuse environment. Large lysimeters are being utilized to determine the difference in leachate quality.

In the third effort (3), a distilled water shake test, the elutriate test, was developed and tested to provide a fast, simple procedure for predicting the escape of pollutants from treated and untreated sludges. The short-term elutriate test results were compared to results of a long-term leaching test using the same treated and untreated sludges. The results of this study are discussed in a report entitled "Elutriate Test Evaluation of Chemically Stabilized Waste Materials," EPA-600/2-79-154, August 1979.

A fourth effort (1) relates to a laboratory assessment of fixation and encapsulation processes for arsenic-laden wastes. Three industrial solid wastes high in arsenic concentration were treated by generic processes in laboratory and by proprietary processes at vendors' facilities. Leaching studies on treated wastes consisting of Shake tests on pulverized samples and on intact monolithic samples were performed to assess the relative safety of each product for disposal. The results of the completed effort will be published in a report entitled "Stabilization Testing and Disposal of Arsenic Containing Wastes".

A fifth on-going effort (6) relates to encapsulating processes for managing hazardous wastes. Techniques for encapsulating unconfined dry wastes are discussed in a report entitled "Development of a Polymeric Cementing and Encapsulating Process for Managing Hazardous Wastes," EPA-600/2-77-045, August 1977. Additional evaluations are currently being performed whereby containers of hazardous waste (i.e., 55 gallon drums) are placed in a fiber glass thermosetting resin casing and covered with a high density polyethylene. The results of these evaluations will be published in three reports entitled "Study of Encapsulate Formation with Polyethylene Resin and Fiberglass for Use in Stabilizing Containerized Hazardous Wastes", "Study of Encapsulation for Securing Corroding 55-Gallon Drums Holding Hazardous Wastes by Welding Polyethylene Resin", and "Study of Encapsulate Formation with Resin by Spray and/or Brush Under Atmospheric Conditions for Use in Management of Containizered Hazardous Wastes".

A sixth on-going effort (3) is to determine how potentially useful sulfur-asphalt binder composites are for stabilization/solidification and disposal of toxic metal bearing wastes. Indications from work carried out on paving material suggest that sulfur-asphalt blends can furnish uniquely desirable properties when used as binders for toxic waste control.

LANDFILL ALTERNATIVES

Due to the concern for environmental impact and economics, alternatives to waste disposal in sanitary landfills and by incineration have been proposed. Alternatives currently being researched by SHWRD include land treatment and surface impoundments.

Land Treatment

The SHWRD program includes research and evaluation of spreading (or incorporating) of industrial hazardous waste onto the land for treatment by biological, chemical, and physical processes resulting from interactions of the soil (and its constitutents) with the waste. The technology is referred to as "land treatment." Land treatment enhances degradation by providing an aerobic soil medium capable of supporting microorganisms and providing exposure to sunrays. The land treatment research program has three basic objectives. These are a) to determine environmental effects from hazardous waste land treatment facilities and their monitoring requirements b) to determine hazardous waste land treatment facility closure requirements and post-closure monitoring requirements c) to develop basic knowledge required to fully understand land treatment of hazardous waste.

One effort (3) is designed to develop a matrix of industrial organic and inorganic, and municipal solid waste streams versus operational parameters. The final matrix of information will be sufficiently complete to develop design and guideline criteria. The results of this completed effort will be published in a report entitled "Field Verification of Land Cultivation/Refuse Farming".

A second effort (3) was aimed at optimizing the operational parameters for the biodegradation of API oil-water separator sludge on the germination and yield of ryegrass in order to generate data on acceptable sludge loading rates and to elicit mechanisms which affect plant responses. Long-term yield reductions largely resulted from impaired water, air and nutrient relations associated with recalcitrant hydrophobic hydrocarbons.

A third effort (6) was the development of a best engineering judgement (BEJ), Permit Writer's Guidance Manual which compiles the information necessary to develop a land treatment facility. This project also offered technical support for the management of a land treatment facility. This manual includes comprehensive background information and criteria for reference by designers, permitting officials, and technical (field) personnel in the area of land treatment. Illustrative case studies unique laboratory methods, and a land treatment glossary are also included. The manual is entitled "Design and Management of Hazardous Waste Land Treatment Facilities ".

A fourth on-going effort (6) evaluates current land treatment data required to support development of and revisions to the best engineering judgement (BEJ), Permit Writer's Guidance Manuals, required in support of RCRA regulations. Research under this agreement will involve a combination of evaluations of available data, laboratory and greenhouse investigations, on using the land as a treatment/management medium for hazardous wastes. Studies will involve determination of effects of food and non-food chain crops, development of crop response curves, determination of soil effects on hazardous pollutant migration, ion exchange capacity effects, soil adsorption and neutralization effects, feasibility of mixing hazardous waste streams, waste preconditioning, and numerous other factors required to better understand land treatment of hazardous waste.

A fifth on-going effort (3) identifies and prioritizes hazardous waste streams likely to be amenable to land treatment as a management alternative, recommends laboratory and field research to fill in significant data gaps, and verifies the environmental acceptability of land treatment as a waste treatment/resource recovery method for a significant fraction of the hazardous wastes generated.

A sixth on-going effort (6) assesses technical requirements for effective closure of hazardous waste land treatment facilities. Effective closure is accomplished when the environment is completely protected from potential adverse effects of the land treatment facility. Although petroleum land treatment facilities will be used in cooperation with the American Petroleum Institute, tests will be designed so that information is applicable to other wastes.

A seventh on-going effort (6) was undertaken to determine the utility of bioassays as a control/monitoring technique for evaluating the operation and engineering performance of hazardous waste land treatment sites. Results will be used to determine hazardous waste land treatment site engineering design and control technology required to prevent movement of potential mutagens from the site.

An eighth on-going effort (6) characterizes the technical and environmental aspects of using land treatment technology for treating tannery waste sludges. The project is a field investigation and evaluation designed to verify information available from laboratory and greenhouse work, and to provide EPA with data on the proper design and operation (including closure) of similar hazardous waste land treatment facilities.

A ninth on-going effort (6) studies active petroleum land treatment sites operating for five years or longer. Core samples will be taken at selected locations, segmented at different levels, and analyzed for various constitutents. Information generated will help evaluate the fate of organics and other contaminants, and their potential migration from hazardous waste land treatment facilities.

Surface Impoundments

The temporary, or permanant retention of liquid hazardous wastes in surface impoundments (i.e., pits, ponds, or lagoons) is an alternative to disposal in a sanitary landfill, which SHWRD is researching. Surface impoundments require special consideration to control vaporization and volatilization in the air.

The initial effort (4) is providing technical information necessary to evaluate a landfill or surface impoundment design in the form of a best engineering judgement (BEJ) Permit Writer's Guidance Manual. The manual is addressing movement of liquid through the final cover and liner materials, the efficiency of the leachate collection system, and volumes of leachate collected. The results of this effort will be published in a manual entitled "Closure of Hazardous Waste Surface Impoundments".

A second on-going effort (4) is investigating mechanisms of chemical movement of pollutants from surface and near-surface impoundments into the air. Methods for estimating air emissions of hazardous chemicals from waste disposal sites are being developed.

UNCONTROLLED SITES/REMEDIAL ACTION

An on-going study by OSW has identified incidence of water well contamination due to waste disposal sites. Seventy-five (75) to eighty-five (85) percent of all sites investigated are contaminating ground or surface waters. In order to determine the best practical technology and economical corrective measures to remedy these landfill leachate and gas pollution problems, a research effort has been initiated (1) to provide local municipalities and users with the data necessary to make sound judgments on the selection of viable, in-situ, remedial action procedures and to give them an indication of the cost associated with such an action. This research effort is being pursued at a municipal refuse landfill site at Windham, Connecticut. This effort consists of three phases. Phase I will be an engineering feasibility study that will determine on a site specific basis the best practicable technology to be applied from existing neutralization or confinement techniques. Phase II will determine the effectiveness, actual field verification, of the recommendations/first phase study. Phase III will provide a site remedial guide to local municipalities and users. The engineering feasibility study has been completed and a report entitled "Guidance Manual for Minimizing Pollution from Waste Disposal Sites," EPA-600/2-78-142, August 1978 has been published. This guidance document emphasizes remedial schemes or techniques for pollutant containment.

The scheme currently installed and monitored at the Connecticut MSW site is a surface capping technique which could be followed by a leachate extraction scheme if required.

A second on-going effort (1) is concerned with the development of a manual on remedial action for hazardous waste landfill sites. The methodology and documentation for this manual will be developed by implementing a remedial program at a hazardous waste landfill site in New Jersey. This program will consist of a quantitative site assessment, selection and design of a remedial system and implementation of that design system.

A third on-going effort (7) is a technology analysis assessing the extent of environmental damage associated with a hazardous waste dump site, and planning alternative programs for remedial action. This effort relates solely to the hazardous waste dump site in Conventry, Rhode Island and is being performed in conjunction with the current effort undertaken by the state of Rhode Island. An analytical report will be prepared which assesses the situation at the Coventry site and evaluates the engineering/technology options for the abatement of the underground chemical contamination at the site. This report will be published and entitled "Use of Remote Sensing Techniques in a Systematic Investigation of an Uncontrolled Hazardous Waste Site".

A fourth effort (7) provides for a survey of on-going and completed remedial action projects. Ten case study sites were selected and these sites visited and inspected for remedial action information. The results of this study are published in a report containing case study summary statistics of each of the sites investigated. The results of this completed effort will be published in a final report entitled "Survey of On-going and Completed Remedial Actions".

A fifth on-going effort (7) is concerned with the assessment of barrel and drum reconditioning to determine environmental impact and to make recommendations for possible improvements in the reconditioning processes. Based on industry characterization and specific facility identification, two facilities will be chosen for sampling and analysis efforts, which will monitor for air, land and water pollutant discharges. Should these efforts show that the facilities tested are not environmentally acceptable, a process design and optimization effort shall be undertaken.

A sixth on-going effort (7) will evaluate and verify several selected concentration techniques for compatibility with the ultimate disposal/detoxification of hazardous materials. One concentration/pretreatment scheme will be selected for further development and subsequent field scale verification with an actual waste stream containing hazardous materials. The results of this effort to date will be published in a report entitled "Concentration Technologies for Aqueous Hazardous Waste Treatment".

ECONOMIC ASSESSMENT

The use of market-oriented incentive (disincentive) mechansims has received very little consideration for pollution control policy in the United States, particularly in the area of hazardous waste management. Economic theory suggests that incremental pricing of waste collections and disposal would reduce the waste generation rate, enhance source separation of recyclable materials, accelerate technological innovation, and minimize total system cost.

One completed effort (8) examined the applicability of cost-risk-benefit analysis and related decision criteria to the management of hazardous wastes. The use of cost-benefit techniques as tools for assisting regulatory policy development was addressed.

A second completed effort (8) has resulted in a report entitled "Cost Comparison of Treatment and Disposal Alternatives for Hazardous Wastes" to be published soon. Unit costs are estimated for sixteen (16) treatment and five (5) disposal techniques applicable to various hazardous wastes. Life cycle average unit costs are presented in both tabular and graphic form.

A third on-going effort (8) periodically updates unit operations cost data for long term remedial action programs at uncontrolled hazardous waste sites.

CONCLUSIONS

The laboratory and field research project efforts discussed here reflect the overall SHWRD effort in hazardous waste disposal research. The projects will be discussed in detail in the following papers. More information about a specific project or study can be obtained by contacting the project officer referenced in the text. Inquiries can also be directed to the Director, Solid and Hazardous Waste Research Division, Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, 26 West St. Clair Street, Cincinnati, Ohio 45268. Information will be provided with the understanding that it is from research in progress and the conclusions may change as techniques are improved and more complete data become available.

PROJECT OFFICERS

All the Project Officers can be contacted through the Solid and Hazardous Waste Research Division (SHWRD), whose address is shown above.

1. Mr. Donald E. Sanning (SHWRD)
   513/684-7871
2. Mr. Richard A. Carnes (IERL)
   513/684-4303
3. Mr. Robert E. Landreth (SHWRD)
   513/684-7871
4. Dr. Mike H. Roulier (SHWRD)
   513/684-7871
5. Mr. Dirk R. Brunner (SHWRD)
   513/684-7871
6. Mr. Carlton C. Wiles (SHWRD)
   513/684-7871
7. Mr. Stephen C. James (SHWRD
   513/684-7871
8. Mr. Oscar W. Albrecht (IERL)
   513/684-4318

IMPROVED TECHNIQUES FOR FLOW OF LIQUIDS THROUGH HAZARDOUS WASTE LANDFILLS

Elfatih Ali
Charles Moore

The Ohio State University
Columbus, Ohio 43210

ABSTRACT

This paper describes research performed to develop techniques for improving predictions of flow of liquids through hazardous waste landfills. Statistical methods are used both to describe the porous media and to solve the differential equations of flow. A practical example is presented.

Introduction

This paper presents a summary of the work completed through December 1980 on the Improved Assumptions for Flow of Liquids in Landfills awarded by the Negotiated Contracts Branch of the U.S. Environmental Protection Agency under Contract No. 68-03-2963.. The contract/award is being monitored by the Ohio State University Research Foundation (OSURF) under the direction of Dr. Charles A. Moore who serves as principal investigator. The OSURF designation for the project is RF712979 U.S. EPA.

The contract is intended to provide an improved state of the art approach for determining the rate at which liquids move through hazardous waste disposal landfills. These improved assumptions will then be used to update the best engineering judgement Evaluation Procedure Manual for Landfill and Surface Impoundment Containment prepared by Geotechnics, Inc.

Background

The present version of the Landfill and Surface Impoundment Evaluation Procedures manual uses highly simplified assumptions regarding the rate at which liquid is transmitted through the waste cell. Specifically, plug flow is assumed. Thus liquid that enters the top of the waste cell is presumed to appear instantaneously at the bottom of the cell. This simplification was predicated on the following:

(1) the state of the art for the flow through extremely heterogeneous media is not well understood,

(2) because hazardous waste disposal practice is still evolving, the manner in which waste is emplaced in the cell is variable, and

(3) innovative disposal schemes are likely to be proposed in the near future.

Scope of the Research

This research project has a rather broad scope -- spanning the gamut from the development of fundamental scientific concepts to the development of specific practical configurations for cell construction.

The first phase of the research consists of developing statistical means for describing the geometric arrangement of wastes placed in disposal cells. The statistical formulation will be abstract in that there will be parameters that can be varied to allow for the simulation of essentially any desired placement geometry for the waste. For example, it will be possible to vary the parameters to simulate disposal in drums, disposal of shredded dry material, disposal of baled dry material, disposal of sludges, etc. The philosophy upon which this first phase is based has the important advantage of allowing the same analytical scheme to be used to describe the geometry of all waste placement configurations whether they be presently used or be proposed for use in the future.

The second phase of the research consists of developing the analytical procedures to determine how liquids flow through the waste. The flow processes to be considered are complex and include:

(1) flow dominated by infiltration wherein capillary forces draw liquid into partially saturated fine grained materials,

(2) saturated Darcy flow wherein gravitational forces predominate and flow is macroscopically laminar, and

(3) flow in large openings where inertia terms predominate.

Although continuum mechanics equations will be developed to describe the flow processes, the solution of the equations will use statistical approaches such as Monte Carlo or random walk schemes. The statistical approaches for solving the equations will be used because of their analytical compatibility with the statistical approaches being used to describe the geometric properties of the porous media.

Impact of Research on Future Disposal Technology

The way in which statistical techniques are used to solve the flow equations in heterogeneous media may have an important philosophical impact on future disposal technology. Ordinarily, a configuration for disposal is preconceived, and the resulting flow characteristics are then analysed. This approach can best be termed "guess and then analyze". If the analysis shows that the flow characteristics do not meet requirements, the design is altered by guessing at a configuration that is likely to perform in a more desirable manner.

The proposed approach to analysis consists of transforming the actual geometrical arrangement of the waste disposal cell into a statistically equivalent but geometrically simpler geometric arrangement called an image domain. The image domain does not look like the landfill cell; however, it has identical behavior from the point of view of its ability to transmit liquids. The flow analysis is actually performed on the image domain.

The philosophical impact of the statistical approach is perhaps most significant when viewed inversely. We can first devise an image domain that meets the desired flow requirements. Then we can use inverse statistical mapping to create one or more real physical geometrical arrangements that have flow properties identical to the image domain which, in turn, is already known to have properties that meet performance specifications. In this manner, we are literally able to create a variety of designs that meet performance criteria. The choice of one particular design from among the alternatives can be based on additional criteria such as cost, preferred local practice, etc.

Results to Date

The results of practical importance achieved to date are, of course, limited because the project is in its early stages. However, this section presents some results that may be of general interest. The configuration to be examined consists of a hazardous waste landfill cell (Figure 1) having dimensions X (width) by Y (height). The landfill is assumed to consist of two materials; waste cells and earth fill. The permeabilities of these two materials are KC and KF respectively. The cells are assumed to be uniformly distributed in the landfill, and the earth cover is considered to have uniform thickness T all around the waste cells.

Both the cells and earth cover materials were considered to be saturated, and the liquid flow is assumed to follow Darcy's Law. Only two dimensional confined flow is considered in this example.

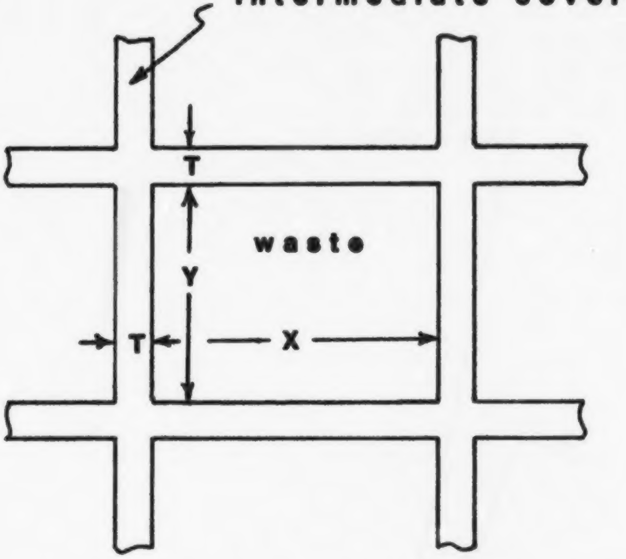


Figure 1. Geometry Assumed for Example Problem.

The flow was analyzed using a random flow model for a deterministic medium. Different landfills were simulated by varying the geometric properties and the permeabilities of the two materials:

R = T/X (ratio of earth cover thickness to cell width)

RK = KC/KF (ratio of permeabilities of cell and earth cover)

A = X/Y (ratio of width to height of cell)

Each landfill was studied and an average equivalent permeability K' was computed.

Initially a square cell geometry (A = 1) was investigated. Figure 2 shows the variation of the normalized permeability (K'/KF) with R for different values of RK. The variation of K'/KF with RK for different R values is shown in Figure 3.

The effect of the shape of the cell itself was then studied. Figure 4 shows the variation of K'/KF with A for different values of RK. In this case the value of R as kept constant at 0.05. (Other values of R were also investigated and the trends obtained were similar to those shown in Figure 4; however, the numerical values were different.)

Discussion of Results

Figure 2 indicates that K' decreases as R increases. The reduction factor obtained here for K' ranged from 1/2 to 1/5. Although the value of the permeability of the waste cell, K', is not known, the permeability of the earth cover materials can be estimated. Hence a change in the value of RK (= KC/KF) can be brought about by changing the value of KF. From Figure 3 we notice that K' increases as RK increases. The magnification factors obtained range from 3 to 15.

The geometrical shape of the waste cell has a considerable effect on K'. If we consider the square cell as the reference shape, and assume that the landfill with square cells has an average equivalent permeability K", then Figure 5 can be constructed. This figure plots a multiplication factor (M = K'/K") as a function of A for different values of R. Two separate regions are apparent in Figure 5:

(1) for A < 1 K' increases as A increases but K' decreases as RK increases, and

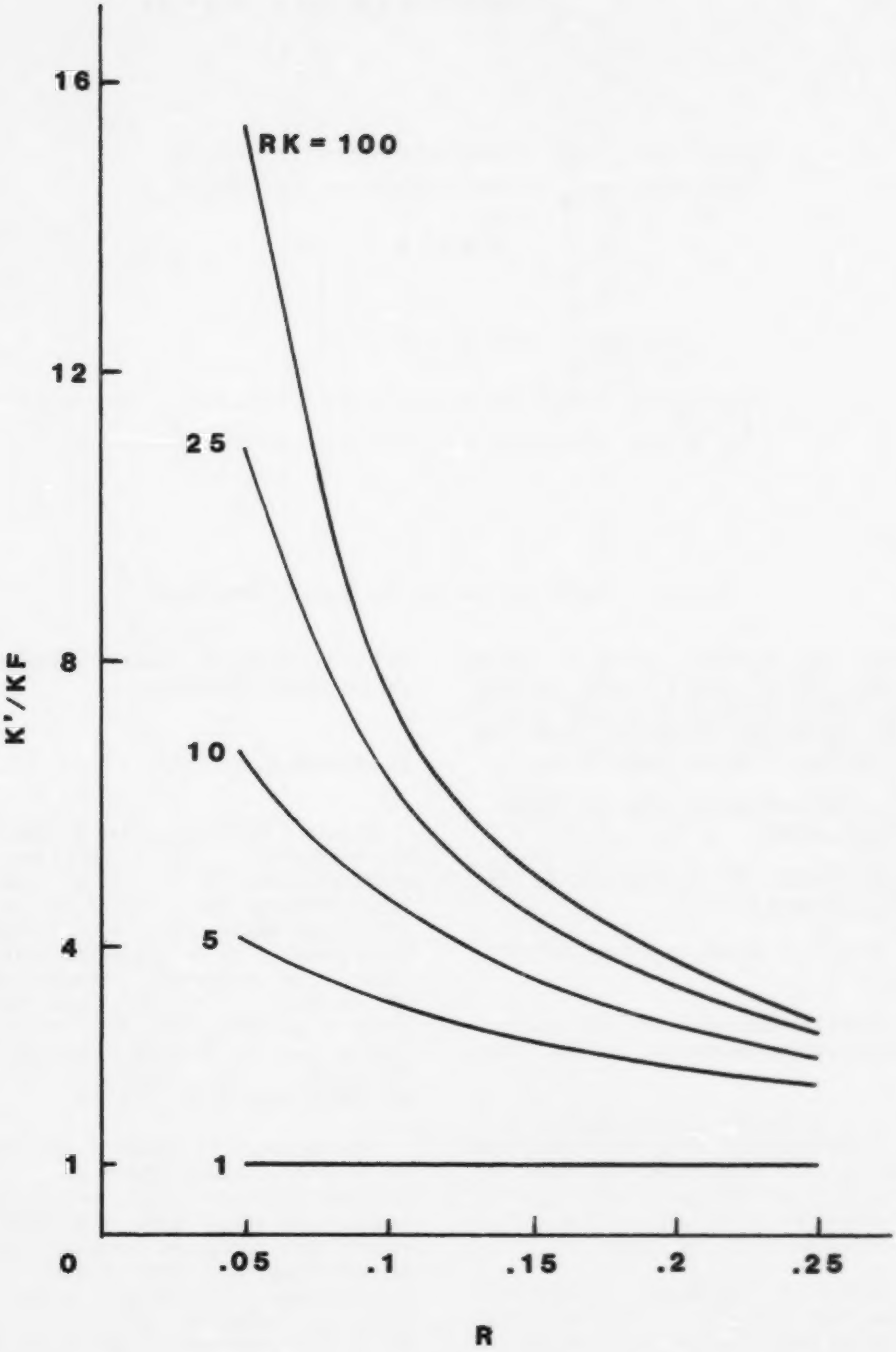


Figure 2. Ratio of Normalized Permeability (K'/KF) as a Function of the Ratio of Cover Thickness to Cell Width (R = T/X) for Different Values of RK

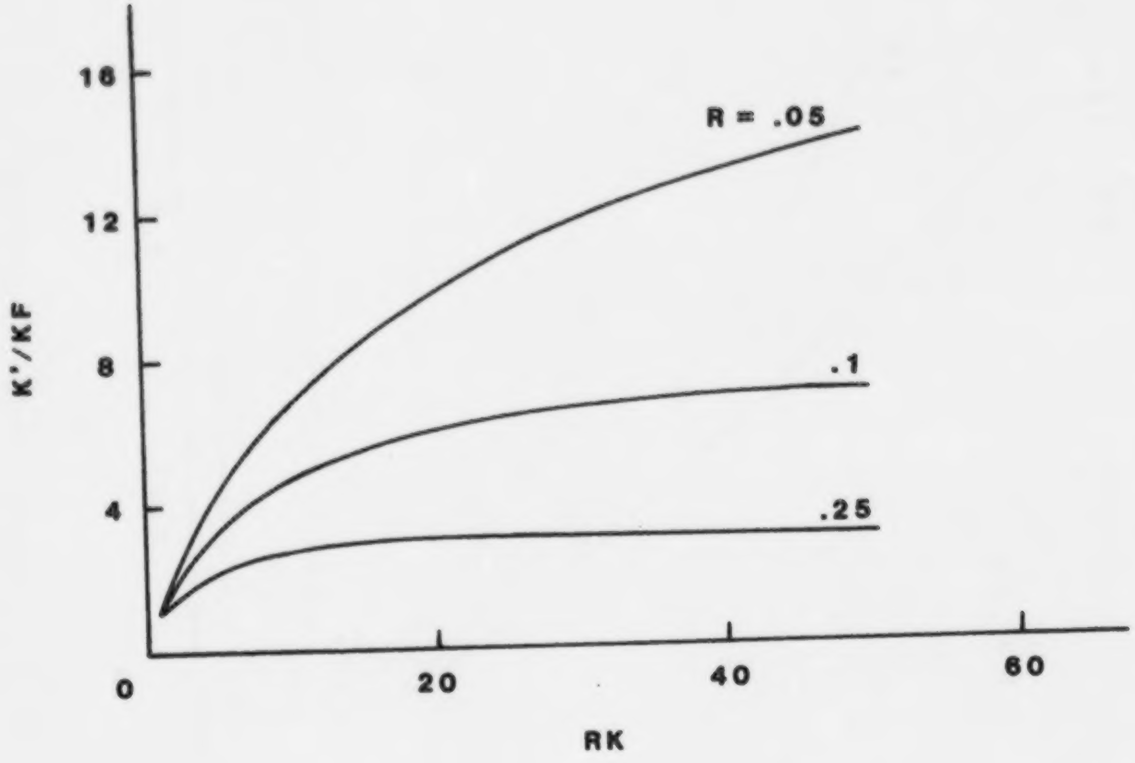


Figure 3. Ratio of Normalized Permeability (K'/KF) as a Function of the Ratio of Permeabilities of Cell and Earth Cover (RK = KC/KF) for Different Ratios of Cover Thickness to Cell Width (R = T/X)

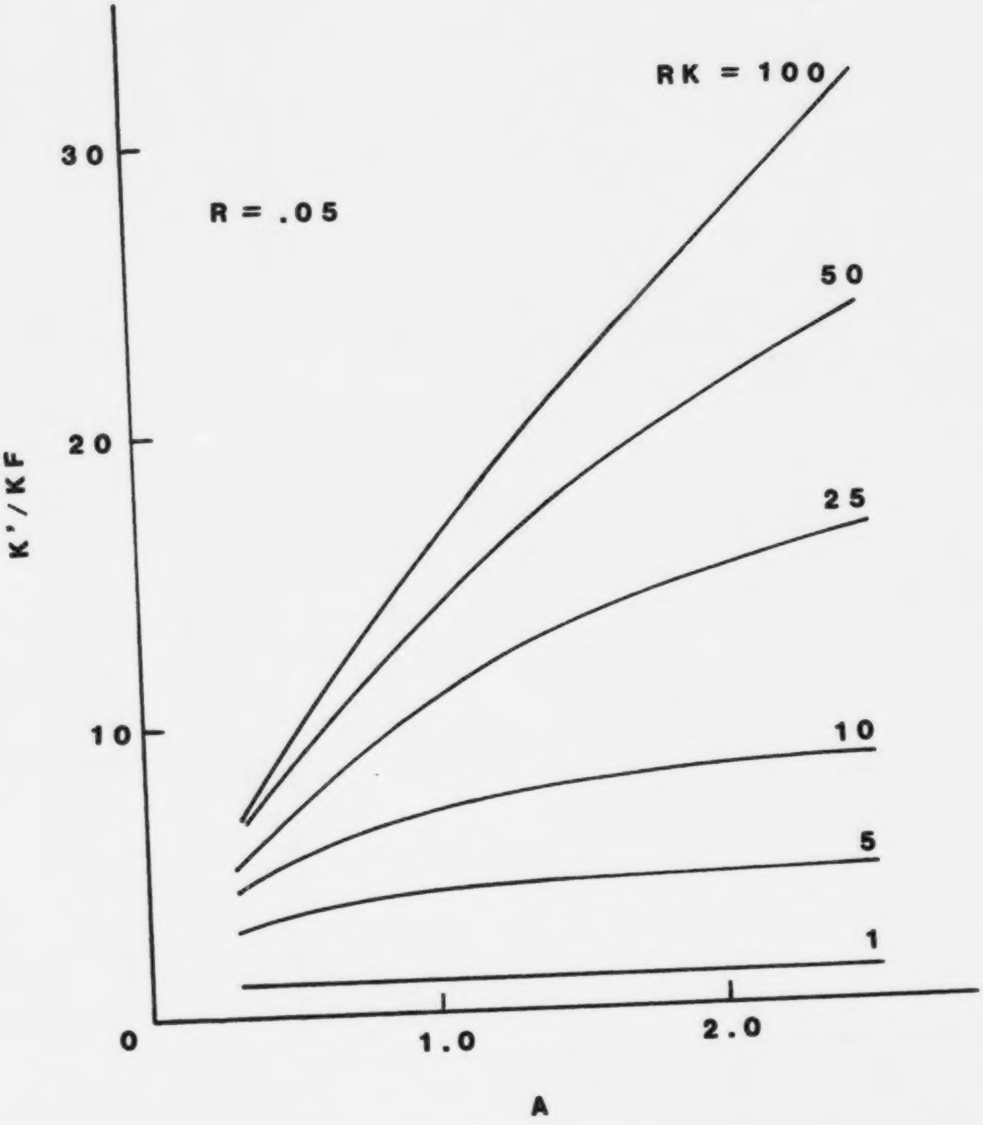


Figure 4. Ratio of Effective Permeability to Permeability of Cover Material (K'/KF) as a Function of Width to Height Ratio (A = X/Y) for Cell and for Different Permeability Ratios (RK = KC/KF)

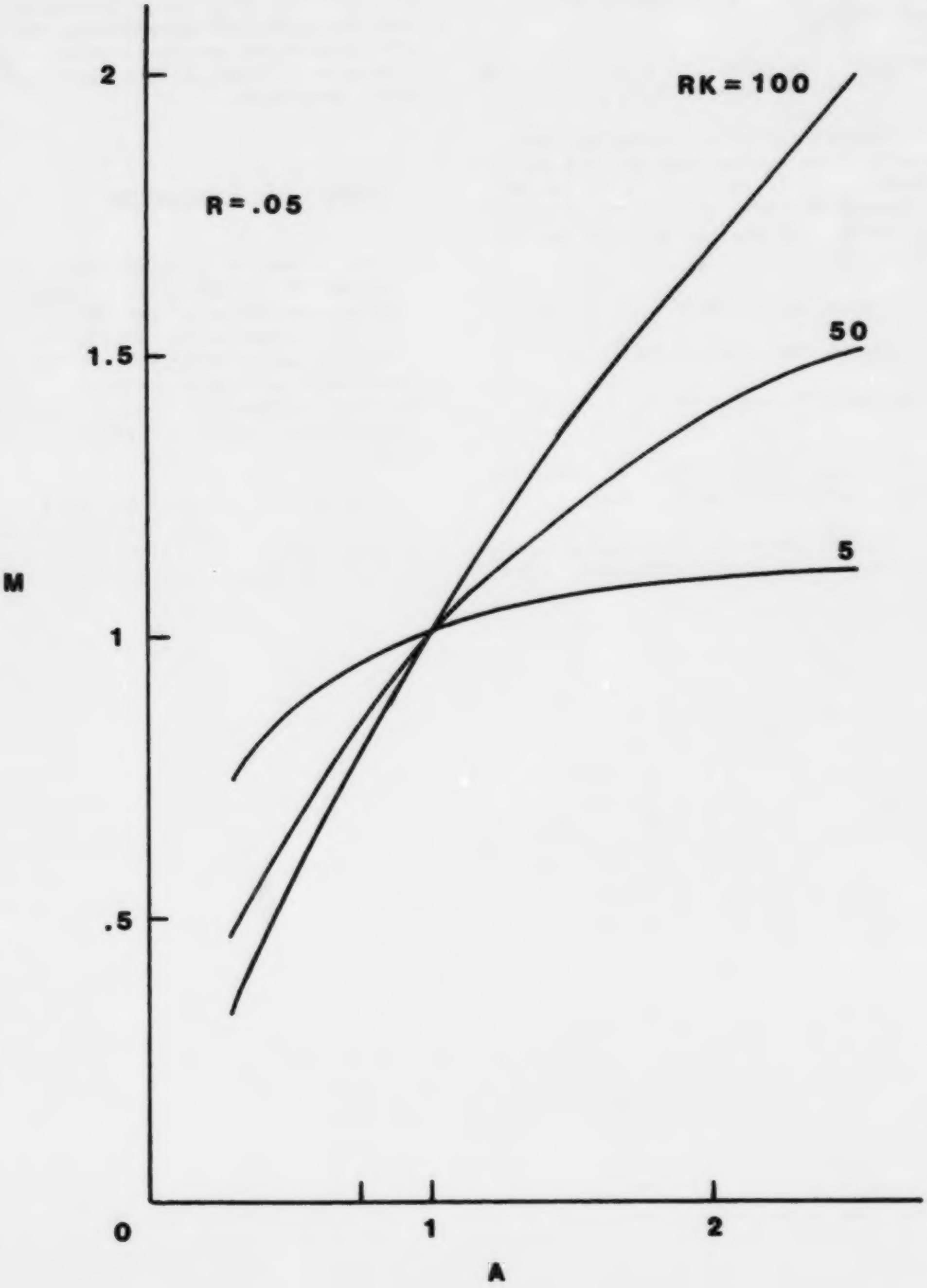


Figure 5. Ratio of Effective Permeability of Square Cell to Effective Permeability (M = K'/K") as a Function of Ratio of Cover Thickness to Cell Width (R = T/X)

(2) for $A > 1$ K' increases as both A and RK increase.

For the case shown in Figure 5, the value of M varied between 0.33 and 2.0.

The results of this investigation can be used to give guidelines for the design of landfills. If the goal is to increase the value of K' then the course of action should be to take one or more of the following steps:

(1) decrease the value of R,

(2) increase the value of RK,

(3) increase the value of A.

If the goal is to reduce K' then the opposite course is to be followed.

The results presented here apply to the simple case of uniform rectangular cells with uniform earth cover thickness. More sophisticated cell geometries, non-uniform cell dimensions and earth cover, and three dimensional flows will be analyzed as the study progresses.

Summary and Conclusions

The research project deals with the development of analytical techniques to improve the analysis and design processes for the transmission of liquids through hazardous waste landfills. The approach being used is highly versatile, and allows for the treatment of innovative as well as conventional waste disposal configurations.

Preliminary results to date indicate that the approach can be used effectively to optimize designs in the single configuration (rectangular cells) described.

DEVELOPMENT OF A SOLID WASTE LEACHING PROCEDURE AND MANUAL

Benjamin C. Garrett, Mary M. McKown, Marvin P. Miller,
Ralph M. Riggin, and J. Scott Warner
Battelle Columbus Laboratories
Columbus, Ohio 43201

ABSTRACT

The Resource Conservation and Recovery Act of 1976 requires the U.S. Environmental Protection Agency to institute a national program to control hazardous waste. One aspect of this program involves the issuing of permits for operating a hazardous waste disposal facility. This paper describes the development of a solid waste leaching procedure manual that could be used in the design of land disposal facilities for hazardous wastes. The manual details laboratory procedures for extracting or leaching a sample of solid waste so that the composition of the laboratory leachate is similar to the composition of leachate from the waste under field conditions. The solid waste leaching procedure in the manual is summarized in this paper, and the major assumptions and rationale critical to the procedure are discussed.

BACKGROUND

The U.S. Environmental Protection Agency will review applications for permits to operate hazardous waste disposal facilities that are subject to the regulations set forth in the Resource Conservation and Recovery Act (RCRA), Section 3004 (40 CFR Part 264). Those individuals involved in the permit writing and review processes will need guidance to aid in evaluating the performance of a disposal facility.

One aspect of this performance evaluation is the determination of the nature of the leachate percolating out of the hazardous waste and into either the underlying soil or a leachate treatment system. This leachate arises from both the loss of liquid present in the waste and the infiltration of natural moisture into the waste. Information on leachate composition will be used in judging the adequacy of a leachate treatment system. This information will also be needed for predicting the impact on groundwater resulting from any leachate seepage from the bottom of the landfill.

The need for leachate composition data has prompted a project that will develop a solid waste leaching procedure and manual. This paper presents a report on that solid waste leaching procedure project and outlines the currently proposed procedure. The objectives and assumptions of the project are discussed, along with the schedule for the preparation and revision of the procedure. The direction and scope of future work on this project are outlined.

OBJECTIVES

The primary objectives of this solid waste leaching procedure project are:

1) The development of a solid waste leaching procedure applicable to the hazardous waste disposal facility process.
2) The preparation of a manual detailing the routine use of the solid waste leaching procedure.
3) The preparation of a technical background document describing the scientific basis and rationale for the steps in the procedure.

The above objectives point out that the project involves laboratory studies both to select a suitable leaching procedure and to incorporate this procedure into a standard laboratory manual. This leaching procedure is being developed for a different purpose than the Extraction Procedure (EP) specified in RCRA Section 3001. Although some of the techniques in the EP may be used, the two procedures will differ substantially.

The schedule that has been set for meeting these project objectives is given in Table 1. The table shows that the solid waste leaching procedure manual is scheduled to go through three revisions prior to publication of the final document. Having several revisions allows both technical peer review of and public comment on the proposed manual, as has been done for the other technical resource documents. In this way, the manual will be improved to reflect suggested changes in either the solid waste leaching procedure itself or the directions given for carrying out that procedure.

TABLE 1. PROJECT SCHEDULE

Date	Item
September 17, 1980	Solid Waste Leaching Procedure Manual, Draft I, Submitted
January 15, 1981	Manual, Draft II, Due
July 31, 1981	Manual, Draft III, Due
January 31, 1982	Manual, Final, Due Technical Background Document, Due

The manual has already gone through one cycle of publication and review(7). This process has resulted in certain improvements in the procedure. Future cycles of publication and review are expected to involve a wider audience of qualified reviewers than did the initial cycle. The product of this extensive reviewing and revising process is expected to reflect current knowledge of leaching behavior of wastes plus best judgement on the art of conducting leachate testing.

LEACHING PROCEDURE

Goals

The solid waste leaching procedure included in the manual is intended to:

- Provide a realistic leachate profile, showing the change in constituent concentration with amount of leaching
- Be site specific
- Be applicable to a variety of solid wastes
- Be usable by minimally trained technicians
- Be understandable by and seem reasonable to supervisory and management personnel lacking a scientific background in solid waste leaching.

Each of these goals reflects the need to have the manual itself be a working document for those personnel involved in the hazardous waste disposal facility design and permit application and review processes. These people need a laboratory procedure that will generate a leachate which accurately predicts the site leachate composition during the life of the waste, hence the goal of providing a realistic leachate profile. Further, the leaching procedure must be site specific so that the procedure can be tailored to reproduce the conditions associated with some identified disposal site.

The manual is likely to be used for testing of any sort of solid waste that is being evaluated for landfill disposal. Therefore, the leaching procedure must be applicable to the wide variety of wastes which might be encountered in such testing.

The manual has been developed to instruct minimally trained technicians. Although such individuals can be assumed to be knowledgeable about general laboratory practices, they may be unfamiliar with techniques used in leachate testing. Furthermore, even though the solid waste leaching procedure might be carried out by technicians, certain management personnel will be entrusted with the responsibility for supervising the actual conduct of this procedure and for interpretation of the results. These personnel must understand the rationale for the leaching procedure specifications given in the manual. Consequently, the manual contains guidance to aid in identifying and understanding the critical aspects of the waste leaching procedure.

The experiences of the users of the manual will indicate whether the goals of the solid waste leaching procedure have been met. The previously discussed schedule for reviewing and revising the manual has been set up to facilitate meeting these goals.

Development

The development of a leaching procedure for inclusion in the manual involved two major stages prior to drafting a specific procedure. Initially the reported leaching procedures as well as the general knowledge of leachate behavior were reviewed. Next the assumptions and limitations peculiar to the hazardous waste disposal facility environment under consideration were identified. Once these stages had been completed, appropriate solid waste leaching procedures were evaluated.

LEACHATE REVIEW

Considerable research into the chemical and physical nature of leachates, primarily from municipal wastes, has taken place within the past two decades, and numerous leaching procedures have been reported. Comprehensive reviews of both leachate behavior and leaching procedures are available(11,14). Ideally, the leaching medium and test conditions used in a leaching test should reproduce the actual leachate and conditions to be encountered at the field disposal site.

The leachate percolating through a particular waste reflects the composition of all the materials through which that leachate has travelled and depends on such site characteristics as annual rainfall volume and composition, evapotranspiration, biological activity, and the nature of the surrounding soil and wastes(11). Because of the diversity of the site conditions that are encountered in the field, no single leaching medium can completely reproduce the composition of the actual leachate to be found in all situations. However, the factors that influence leaching medium composition have been enumerated (Table 2), and their relative influence on leaching activity can be estimated.

TABLE 2. CRITICAL FACTORS IN A LEACHING PROCEDURE

- I. Leaching Medium Composition
  - A. Proton and Electron Environment
    - 1) pH
    - 2) Redox potential (pε or Eh)
    - 3) Ionic strength
    - 4) Buffering capacity
  - B. Presence of Solubilizing Agents
    - 1) Complexing and chelating agents
    - 2) Colloidal constituents
    - 3) Organic constituents
- II. Leaching Test Conditions
  - A. Contact Area/Particle Size
  - B. Method of Mixing
  - C. Mixing Time
  - D. Temperature Control
  - E. Number of Leachings on the Same Solid
  - F. Number of Leachings on the Same Liquid
  - G. Solid to Liquid Ratio

The predominant characteristics of a leaching medium that directly relate to leaching ability are the proton and electron environments(10,14,19), and the presence of solubilizing agents(16,17). The proton and electron environments have been determined for natural environments and landfill leachates by measuring the pH, redox potential, ionic strength, and buffering capacity(1,2,13). Solubilizing agents include constituents such as complexing and chelating agents (hydroxyl ion, ammonia, EDTA), colloidal constituents (micelles or surfactants), and organic constituents (melanic materials, humic acids). Some of these agents can have a profound effect upon the mobility of inorganic and organic constituents of the waste, even when the agents are present at low concentrations. Although most analyses of field leachates have failed to examine the possible presence of such agents, some more recently developed leaching media have incorporated solubilizing agents(12,20).

Two groups of leachate behavior reports were especially useful in selecting candidate leaching procedures for further evaluation. The report of Lowenbach provides a detailed summary of the test conditions for over 30 proposed leaching procedures. These leaching tests were evaluated by Lowenbach with regard to the critical factors given in Table 2.

The studies of Ham and associates provide a comprehensive evaluation of the effects produced by systematically varying each of the leaching conditions given in Table 2.

ASSUMPTIONS AND LIMITATIONS

Three assumptions have been made regarding the solid waste and its associated disposal facility that are being evaluated by means of this solid waste leaching procedure manual: (1) the disposal facility is a monofill, (2) the site is engineered to be secure, and (3) information is available on site conditions.

Monofill

The solid waste leaching procedure is oriented toward a monofill situation in which a single type of solid waste is disposed at the site. Any waste type will be compatible with the procedure, providing a representative sample is obtained. The extension of the procedure to mixed fills, in which a second type of solid waste is disposed on top of an existing waste, is being studied.

Secure Site

A secure site is engineered to control the movement of water around, into, through and out of the site. The rate of movement may be controlled depending on the extent of protection that is desired. This assumption of a secure site seems reasonable and allows the expected infiltration of moisture during operation and prior to final capping of the fill to be predicted reliably. What the site is designed to do must be known in order to make reliable predictions.

Site Data

The manual user is assumed to have access to disposal site specific information for the site where the solid waste will be disposed. This information includes meteorological and engineering data. Meteorological data involves average and extreme monthly precipitation volumes and precipitation composition. The disposal site engineering data that are likely to be needed and are assumed to be available include the expected surface area and depth of the site, the anticipated schedule for disposal activities, and the intermittent soil cover to be used. These site data are needed for adequate interpretation of the test results.

METHOD

The solid waste leaching procedure developed for use in the manual is shown schematically in Figure 1. This procedure closely resembles Procedure R of the standard leaching test developed by Ham, et al. (10,11) and involves repetitively leaching the same sample of solid waste, using a fresh portion of leaching medium for each repetition.

Procedure R was designed principally to estimate the total amount of leachable species to be released from a unit mass of solid waste. The users of this manual for testing solid wastes will be interested not only in the total amount released but also in the profiles of the leachate constituents. The profile for any leachate constituent will indicate the concentration or mass of that constituent likely to be present in the leachate and the time period, in terms of total volume of leachate produced, when that constituent will be present at any particular concentration or mass.

The method of Procedure R allows this sort of profile to be generated and, hence, was taken for further development with the manual. However, certain changes have been made to tailor that method to fit the intended uses of the manual. The product of these changes is the leaching procedure whose test conditions are described below.

TEST CONDITIONS

Sample

A representative sample of the solid waste under consideration for landfill disposal is used together with a sample of the soil if any is to be used in the fill as an intermittent cover.

A significant aspect to this procedure is the requirement to include a sample of the intermittent cover soil along with the solid waste for testing. This soil should be of the same type and be present in the

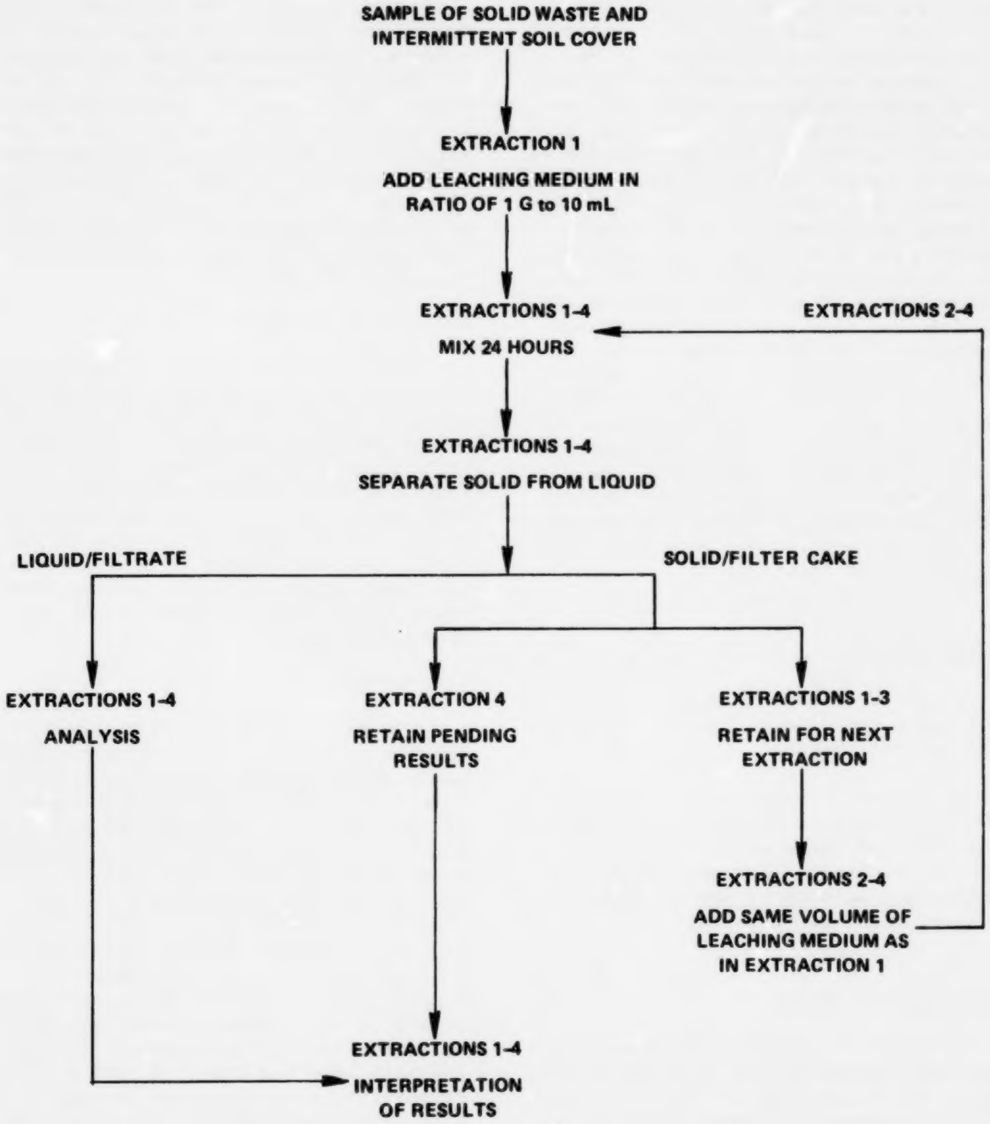

SAMPLE OF SOLID WASTE AND INTERMITTENT SOIL COVER
EXTRACTION 1
ADD LEACHING MEDIUM IN RATIO OF 1 G to 10 mL
EXTRACTIONS 1-4
MIX 24 HOURS
EXTRACTIONS 2-4
EXTRACTIONS 1-4
SEPARATE SOLID FROM LIQUID
LIQUID/FILTRATE
SOLID/FILTER CAKE
EXTRACTIONS 1-4
ANALYSIS
EXTRACTION 4
RETAIN PENDING RESULTS
EXTRACTIONS 1-3
RETAIN FOR NEXT EXTRACTION
EXTRACTIONS 2-4
ADD SAME VOLUME OF LEACHING MEDIUM AS IN EXTRACTION 1
EXTRACTIONS 1-4
INTERPRETATION OF RESULTS

FIGURE 1. SOLID WASTE LEACHING PROCEDURE FLOW SCHEME

same proportion as that which will be encountered at the disposal site. The ability of soils to alter the mobility of species in leachates is well known and has been studied extensively for various types of soils and wastes. For example, the extent to which trace inorganic constituents of leachates are attenuated is directly related to the amounts of clay and iron and manganese hydrous oxides in the soil(6,9); and attenuation of organic compounds such as PCBs is directly related to the organic carbon content of the soil(8). Furthermore, the soil type influences the complexing agents and colloidal constituents present in a leachate and soil mixture. Because of the importance of the amount and type of soil that is mixed with a solid waste, this procedure specifies including the soil with the waste in the sample to be leached. A possible extension of this procedure is to use it with various soil types in order to select the best type and optimal amount for inclusion with the solid waste. Obviously, where the solid waste disposal protocol calls for the use of no soil during active filling, then no soil is used with the solid waste sample for leaching.

Leaching Medium

Distilled, deionized water is used unless another medium can be justified on a site specific basis.

The choice of water as the leaching medium is consistent with the assumption of a monofilled solid waste. Where environmental conditions warrant, the use of alternate media, such as one to duplicate acid rain, might be justified.

Solid to Liquid Ratio

The solid to liquid ratio should be one to ten (weight/volume on a wet weight basis). The true solid to liquid ratio that a solid waste will experience is highly site dependent and very difficult to forecast precisely. In most cases the ratio will be one of a large amount of solid per unit volume of leachate. The specified ratio of 1:10 does not truly reflect the likely field conditions; rather it is a workable amount that will allow sufficient liquid for proper mixing and constituent analysis.

Time Per Leaching

The approximate time per leaching is 24 hours. The time specified for each leaching should ideally be sufficient to allow equilibrium to be attained. However, due to the diversity of constituents and effects, no reasonable time per leaching is likely to be satisfactory for all situations. Therefore, the specification of leaching time has to be made out of consideration of factors other than attainment of equilibrium. A time of approximately 24 hours is normally convenient for laboratory scheduling and is consistent with the time specified for other related leaching procedures(11,18).

Numbers of Leachings

Four leachings should be sufficient to allow definite trends in a leachate constituent level (increasing, decreasing, or no change) to be noticeable. However, the solid waste plus soil sample used for the four leachings is retained pending the analyses of the filtrates and interpretation of the results. In the event the results warrant further leachings, then the leaching cycle can be started with the saved sample and can be continued for as many repetitions as desired.

Temperature

The temperature should be normal room/laboratory temperature. The temperature has a decided effect upon the solubility, rate of reaction, and, perhaps, leaching of most species. Although ambient temperatures to be expected at land disposal sites range from extremely cold (∿-40°C) to very hot(∿45°C), the temperatures for the leachates associated with these sites are likely to be less varied. The overlaying soil and waste layers with which the leachate is associated have a dampening effect on variations in temperature(5). Consequently, the temperature for the leachate emerging from the bottom of a disposal site is likely to be that of the soil at the same depth. The limits on seasonal fluctuations in soil temperature at various depths are probably obtainable from disposal site data or can be measured during preliminary site investigations. If the expected temperatures differ substantially from the range of normal laboratory temperatures, then the use of other temperatures is justified. In any event, the temperature used in the leaching procedure should be close to that expected for the site leachate.

Mixing Technique

Any mixing device that will impart sufficient agitation to the mixture such that stratification of the leaching medium-sample mixture is avoided and sample surfaces are continuously brought into contact with the leaching medium.

The method of agitating or mixing the leaching medium-sample mixture has been studied to determine which method offers the best combination of ease of operation and extent of liquid-solid contact. Ham, et al., investigated five methods of mixing: mechanical and manual shaking; mechanical stirring; swing shaking (180 degree swing); and variable pitch rotary mixing. Their results showed comparable levels for inorganic constituents using the various methods. However, thier recommendation was to use the rotary mixer because visual observations of the methods showed that the other methods occasionally failed to wet the waste uniformly(11).

Epler, et al., of Oak Ridge National Laboratories have studied mechanical stirrers and have found that the major problems included: binding of the stirring blade by solid particles; movement of the stirred vessel; stalling of the stirring motor; uneven blade alignment; and sample grinding(3). They have designed a stirrer that eliminates or reduces these problems (4); this unit is to be evaluated for suitability for use in the extraction procedure (EP) of the U.S. EPA Toxicity Test.

A recent study completed for the U.S. EPA compares the operation of the stirrer and rotary mixer (NBS-design tumbler). The results show that the rotary mixer yields better precision than the stirrer (15).

The specification given in the solid waste leaching procedure in the manual follows that contained in the EP of the U.S. EPA Toxicity Test(18). Currently only the rotary mixer meets these criteria for preventing stratification and ensuring continuous liquid-solid contact; however, other methods for mixing are being evaluated for approval for use with this EP.

Sample Particle Size and Surface Area

The surface area should be ≥ 3.1 cm^2/g or sized to pass through a 9.5 mm standard sieve, unless it is a monolithic waste.

The sample particle size and surface area to be used in this procedure is controlled by requiring the sample to be reduced until it meets either the sieving test or the specified surface area of 3.1 cm^2/g or greater. This requirement is designed to approach the conditions likely to be encountered in the field disposal environment due to mechanical filling operations and weathering, and it is consistent with the Federal EP. Some wastes are naturally monolithic. These will not have their particle size reduced as this would cause them to be more leachable than under field conditions. Any waste passing the Structural Integrity Procedure (as given in Reference 18) will be considered to be monolithic and will be tested as a whole rather than at a reduced particle size.

FUTURE WORK

Plans for future work on this project include

1) Revising the drafts of the manual in response to changes that are suggested during the public and peer review periods.
2) Continuing laboratory studies to provide the scientific basis and rationale for the leaching procedure, especially
    a) development of an internal standard for users to check grasp of technique
    b) determining the significance of layers of same waste but of different ages
    c) studying the effect on leachate composition of passage of water through soil cover before contact with the waste.
3) Collecting data from other field and laboratory studies for validating the procedure.

Changes to the proposed solid waste leaching procedure result from both internal comments and external review. As our own experience with solid waste leaching tests increases, we can anticipate alterations that might be suggested. Other changes may come from the general scientific community due to its growing experience with the required Federal extraction procedure that is a part of RCRA. The Federal EP and this solid waste leaching procedure differ in certain significant aspects of both their intended use and their experimental design. For example, the EP is a fundamental part of the required process for determining whether a waste is hazardous within the meaning of RCRA. The EP was designed to consider co-disposal situations and, hence, uses an acidic leaching medium. In contrast, this solid waste leaching procedure is intended to be an adjunct to the hazardous waste disposal facility permitting process and is aimed toward assessing the nature of the leachate to be produced from that disposal site. Co-disposal with municipal waste has been purposefully excluded from the experimental design of this procedure. However, both procedures involve similar basic concepts regarding leachate production. Because of these similarities, other changes may come about as the general scientific community gains experience with the EP. Increased testing and evaluating of that procedure when used on a wide variety of solid wastes and by many different kinds of users may point out improvements that should be adopted not only for the EP but also for this solid waste leaching procedure.

A substantial area for future work involves continuing the laboratory studies that are investigating the validation and verification of this procedure. In particular, the correlation between the composition of a laboratory-generated leachate from a specific waste and that of a leachate generated from the same waste when it is leached under large-scale pilot conditions or under field conditions is being investigated.

As a part of this correlation study, field samples from an existing solid waste disposal site have been collected. The samples collected included disposal site leachate, solid waste, and groundwater from perimeter wells. The solid waste has been subjected to one solid waste leaching procedure; the results are inconclusive. Further work with these samples is necessary prior to interpreting the results. Samples from other solid waste sites are being sought.

In addition, controlled column leaching studies of metal finishing wastes are to be initiated by IERL-Cincinnati in 1981. Our participation in these studies will consist of using the proposed solid waste leaching procedure to generate leachate constituent profiles which can be compared to the profiles for the leachate collected from the columns.

Positive correlation between laboratory leaching tests and field leaching is an essential part of the development of the leaching procedure. Such correlation will allow those individuals involved in the hazardous waste disposal facility permitting process to have confidence that the results of the laboratory test are indicative and representative of what will occur in the field.

ACKNOWLEDGEMENTS

The work which is reported in this paper is being performed under Contract Number 68-03-2970, "Leaching Procedure Manual", with the U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory, Cincinnati, Ohio.

The authors gratefully acknowledge the support and help of Dr. Mike H. Roulier, Project Officer.

REFERENCES

1. Baas Beckling, L.G.M., I. R. Kaplan, and D. Moore. 1960. Limits of the natural environment in terms of pH and oxidation-reduction potentials. J. Geol. 68:243-284.

2. Chian, E.S.K. and F. B. deWalle. 1977. Evaluation of leachate treatment. Volume 1 Characterization of Leachate. EPA-600/2-77-186a, U.S. Environmental Protection Agency, Cincinnati, Ohio. 226 pp.

3. Epler, J. L., et al. 1979. Toxicity of Leachates. IAG No. DOE-IAG-40-646-77/ EPA-IAG-78-D-X0372. Interim progress report to U.S. Environmental Protection Agency. Oak Ridge National Laboratory, Oak Ridge, Tenn.

4. Epler, J. L., et al. 1980. Toxicity of Leachates. EPA-600/2-80-057. U.S. Environmental Protection Agency, Cincinnati, Ohio. 142 pp.

5. Fluker, B. J. 1958. Soil temperature. Soil Sci., 86:35-46.

6. Fuller, W. H. 1978. Investigation of Landfill Leachate Pollutant Attenuation by Soils. EPA-600/2-78-158. U.S. Environmental Protection Agency,

Cincinnati, Ohio. 239 pp.

7. Garrett, B. C., M. M. McKown, M. P. Miller, R. M. Riggin and J. S. Warner. 1980. Manual for Solid Waste Leaching Procedure. Contract No. 68-03-2970. Draft report to U.S. Environmental Protection Agency. Battelle-Columbus Laboratories, Columbus, Ohio.

8. Griffin, R. A. and E.S.K. Chian. 1980. Attenuation of Water-Soluble Polychlorinated Biphenyls by Earth Materials. EPA-600/2-80-027. U.S. Environmental Protection Agency, Cincinnati, Ohio. 101 pp.

9. Griffin, R. A. and N. F. Shrimp. 1978. Attenuation of Pollutants in Municipal Landfill Leachate by Clay Minerals. EPA-600/2-78-157. U.S. Environmental Protection Agency, Cincinnati, Ohio. 157 pp.

10. Ham, R. K., M. A. Anderson, R. Stanforth and R. Stegmann. 1978. The development of a leaching test for industrial wastes. In: Land Disposal of Hazardous Wastes, Proceedings of the Fourth Annual Research Sumposium, San Antonio, Texax, March 6-8, 1978. EPA-600/9-78-016. U.S. Environmental Protection Agency, Cincinnati, Ohio. pp 33-46.

11. Ham, R., M. A. Anderson, R. Stegmann and R. Stanforth. 1979. Background Study on the Development of a Standard Leaching Test. EPA-600/2-79-109. U.S. Environmental Protection Agency, Cincinnati, Ohio. 274 pp.

12. Ham, R. K., M. A. Anderson, R. Stegmann and R. Stanforth. 1979. Comparison of Three Waste Leaching Tests. EPA-600/2-79-071. U.S. Environmental Protection Agency, Cincinnati, Ohio. 234 pp.

13. Johansen, O. J. and D. A. Carlson. 1976. Characterization of sanitary landfill leachates. Water Research, 10:1129-1134.

14. Lowenbach, W. 1978. Compilation and Evaluation of Leaching Test Methods. EPA-600/2-78-095. U.S. Environmental Protection Agency, Cincinnati, Ohio. 111 pp.

15. McKown, M. M., J. S. Warner, R. M. Riggin, M. P. Miller, R. E. Heffelfinger B. C. Garrett, G. A. Jungclaus and T. A. Bishop. 1980. Development of Methodology for the Analysis of Solid Wastes. Contract No. 68-03-2552. Draft final report to U.S. Environmental Protection Agency. Battelle-Columbus Laboratories, Columbus, Ohio.

16. Means, J. L., D. A. Crerar and J. O. Duguid. 1978. Migration of radioactive wastes: radionuclide mobilization by complexing agents. Science, 200:1477-1481.

17. Means, J. L., T. Kucak and D. A. Crerar. 1980. Biodegradability of NTA, EDTA, and DTPA and environmental implications. Envir. Poll., Series B, 1:45-60.

18. Office of Solid Waste. 1980. Test Methods for Evaluating Solid Wastes. SW-846. U.S. Environmental Protection Agency, Washington, D.C.

19. Rai, D., R. J. Serne and J. L. Swanson. 1980. Solution species of plutonium in the environment. J. Environ. Qual., 9:417-420.

20. Stanforth, R., R. Ham and M. Anderson. 1979. Development of a synthetic municipal landfill leachate. J. Water Poll. Control Fed., 51:1965-1975.

BEHAVIOR OF Cd, Ni, AND Zn IN SINGLE AND MIXED COMBINATIONS IN LANDFILL LEACHATES

W.H. Fuller, A. Amoozegar-Fard, E. Niebla, and M. Boyle
Soils, Water and Engineering
University of Arizona
Tucson, Arizona 85721

ABSTRACT

This describes a segment of a research program designed to develop mathematical models that can be used as field-oriented tools to predict migration rates through soils of metals contained in landfill-type leachates. In this phase, the concepts of the Lapidus and Amundson model were used along with actual data collected from soil columns experiments conducted under controlled laboratory conditions. Simple mathematical equations are presented for predicting migration rates of Cd, Ni, and Zn contained singly and in mixed combinations in landfill-type leachates through soils of variable physical and chemical characteristics. The migration behavior of Cd, Ni, and Zn was not significantly different whether contained singly or in mixed combinations in the leachates. Field use is discussed.

INTRODUCTION

The Lapidus and Amundson mathematical model has shown promise as a concept in the prediction of movement of Cd, Ni, and Zn from landfill-type leachates through soils (O'Donnell et al., 1977 and Fuller et al., 1979). The cadmium prototype was presented in an earlier paper (Fuller et al., 1979) in the attempt to provide a user-oriented predictive tool. Refinements in the mathematics of the multitude of factors influencing metal migration rates were necessary before the final presentation of equations for Cd, Ni, and Zn could be made with confidence. No two metals respond (attenuate) identically to the same set of soil and leachate characteristics. Moreover, the question of Cd, Ni, and Zn interaction had to be resolved. Although a great volume of data relating to this question was available earlier, computer testing was incomplete.

Soil and broad leachate properties that most influence Cd, Ni, and Zn attenuation have been quantitatively measured as previously described in detail (O'Donnell et al., 1977; Korte et al., 1976: and Fuller, 1977, 1978). These measurements are in the form of stochastic functions of specific properties of soil - leachate-metal systems. The plan is to match theoretical curves describing selected metal movement in soil columns under controlled conditions of saturated flow with actual data. Such a match gives rise to specific values for the theoretical parameters in the Lapadus and Amundson model. These parameters can be translated directly into a migration rate for a particular element (metal).

Variables introduced into the multiple regression analysis are: clay, silt, sand, hydrous oxides of iron called "free iron oxides" (FeO), Total Organic Carbon (TOC), soluble salts (SALT) primarily the inorganic salts of Ca, Mg, Na, K, Cl, and SO$_4$.: clay^2, silt^2, (FeO)^2, (TOC)^2, salt^2, clay x silt, clay x FeO, clay x sand, clay x TOC, silt x FeO, silt x TOC, silt x salt, FeO x TOC, sand x silt, sand x FeO, sand x TOC, sand x salt.

OBJECTIVE

The objective is to determine the long-range, steady-state migration rates of Cd, Ni, and Zn contained in landfill-type leachates and to arrive at simple formulas that will predict migration rates. This objective was extended to include single and multiple metal enrichment systems for Cd, Ni, and Zn.

APPROACH

Because of the great variabilities associated with soil and geologic materials under field conditions, the examination of metal migration is difficult and time consuming. Useful data for screening purposes may be obtained through the use of soil columns in the laboratory (Fuller, 1977, 1978; Fuller et al., 1979), while avoiding the multitude of problems of field conditions. The user-oriented predictive equations may then be tested by field experimentation for further verification and necessary refinements. Our approach, therefore, is to use soil column studies in association with mathematics as applied to the concepts of the Lapidus and Amundson model.

Many models can be used to describe metal transport through soil (Van Genuchten, 1978; Van Genuchten and Wierenga, 1976; and Fuller et al., 1979). All have some unknown parameters which must be evaluated from experimental data. When the solution is complicated, tedious computer work is required. The Lapidus and Amundson model and its solution has an advantage in simplicity relative to others we have considered (O'Donnell et al., 1977) and it has an analytical representation in contrast to Davidson et al. (1975), and Selim and Mansell (1976). These latter authors considered solute flow in finite columns where the solute and adsorbate followed as instantaneous equilibrium relationship. Skopp and Warrick (1974) considered the soil to be composed of a mobile and stagnant region where the solute adsorption is a diffusion controlled process. Van Genuchten and Wierenga (1976) considered the soil to be composed of several regions. The solute adsorption, however, was considered to be a function of the concentration gradient between the mobile and stagnant regions. Models by Selim and Mansell (1976), and Davidson et al. (1975), had numerical solutions.

The Lapidus-Amundson mathematical model is:

$$\frac{\partial c}{\partial t} + \frac{1}{\alpha}\frac{\partial n}{\partial t} = D\frac{\partial^2 c}{\partial z^2} - v\frac{\partial c}{\partial z} \qquad (1)$$

where:

c = concentration in soil solution (M/L^3)

v = convective (pore water) velocity (L/T)

D = diffusion coefficient (L^2/T)

α = fractional pore volume of soil (L^3/L^3)

n = amount adsorbed per unit volume of soil (M/L^3)

z = vertical distance (L)

t = time (T)

The term $\partial n/\partial t$ describes a linear, non-equilibrium adsorption and is assumed to be

$$\partial n/\partial t = K_1 c - K_2 n \qquad (2)$$

where K_1 and K_2 are forward and backward reaction rates ($1/T$), respectively.

The boundary and initial conditions for a steady input concentration (c_0) are:

$$c = c_0 \quad , \quad z = 0 \quad , \quad t > 0 \qquad (3a)$$

$$\left.\begin{array}{l} c = 0 \\ n = 0 \end{array}\right\} \quad , \quad t = 0 \quad , \quad z > 0 \qquad (3b)$$

The solution to Eqs. (1) and (2) subject to (3a) and (3b) is

$$c = c_0 \exp(vz/2D)\left[F(t) + K_2 \int_0^t F(t)dt\right] \qquad (4)$$

where

$$F(t) = [\exp(-K_2 t)] \int_0^t \{I_0[2\sqrt{K_1 K_2 \beta(t-\beta)/\alpha}]$$
$$\exp[-z^2/4D\beta - \beta d]\cdot[z/2\sqrt{\pi D\beta^3}]\}d\beta$$

with $d = v^2/4D + K_1/\alpha - K_2$. I_0 is the modified Bessel function of the first kind of order zero. The term c/c_0 is referred to as relative concentration, C, and is a function of z and t, and contains the parameter v, α, D, K_1 and K_2.

The Lapidus-Amundson model was formulated to describe the effect of longitudinal diffusion in ion exchange and chromatographic columns, where the chemical and physical parameters are uniform and well controlled; and the system is relatively simple. In a soil-leachate system, the number of parameters increases greatly, and their interrelationships are much more complex. The advantage of the Lapidus-Amundson model is that it combines all unknown or immeasurable parameters into three unknowns, D, K_1, K_2, which can be determined from the experimental data as described below. It would be impossible to determine the spatial interrelation between all the different physical and chemical sites in the soil-leachate system. By applying the Lapidus-Amundson model, the net effect of the chemical nature of the leachate on the forward and backward reaction rates at a multitude of different adsorption sites is combined into an effective forward and backward reaction rates for the particular conditions of the soil-leachate system in the experiment. Similarly, an effective diffusion coefficient is determined, or a diffusion-dispersion coefficient since the effects of diffusion-dispersion combine in one variable.

Miscible displacement theories and experimental data indicate the solute profile is not one of piston displacement, but rather is a smooth distribution of concentrations (Nielsen and Biggar, 1962). In addition, different relative concentrations appear to travel at different rates (Figure 1). Since the velocity of a particular concentration ratio is a function of distance, it follows that the shape of the experimental breakthrough curve will also be a function of z. However, the model predicts that for $z > 10$ cm the velocity of a particular relative concentration approaches an asymptotic value; i.e., steady-state velocity for any relative concentration has been achieved by a depth of 10 cm (Figure 1).

Eight soils representing five of ten major soil orders were used to make 10-cm soil columns which were leached with two municipal solid waste leachates (Fuller, 1978) whose salt contents had been altered to varying degrees.

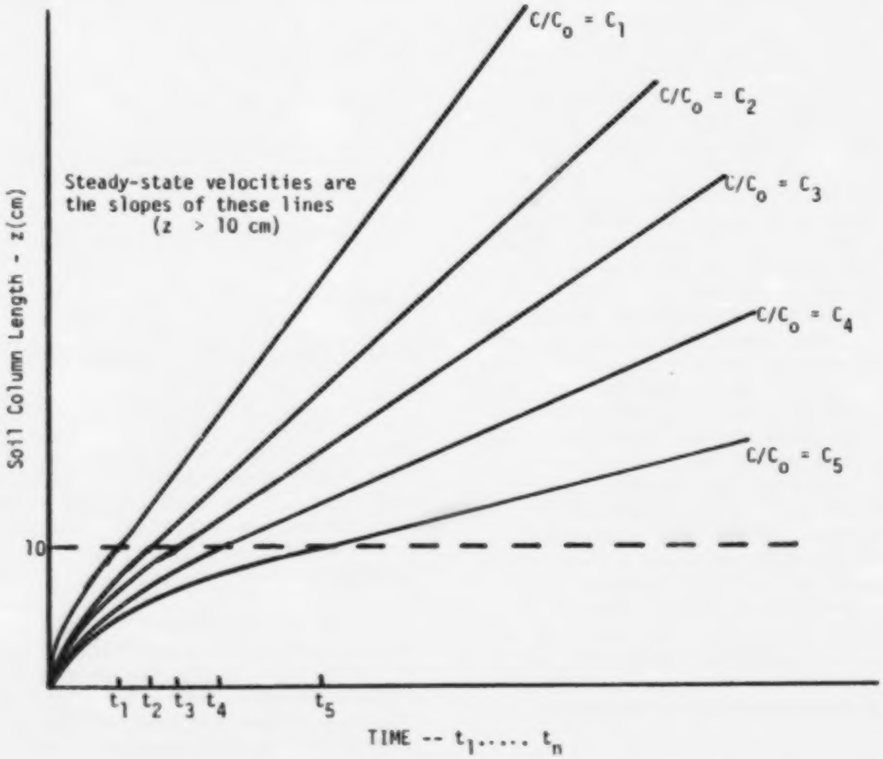


Figure 1. Trajectories of different relative concentrations. (Plot of $z = z(t)$, where $z = z(t)$ satisfies $c(t,z(t)) = C_i$, $i = 1,2,3,4,5$.

In the application of the model, v is estimated by v_d/α where v_d is the Darcian velocity. The variables α, c, c_0 are easily measured. Using these measurable parameters the values of D, K_1, K_2 are selected to give the closest match between the breakthrough curve predicted by the model and the experimental breakthrough observed in the column experiments. A variable metric minimization routine (Davidon, 1959) was employed to find the location of the minimum of the sum of squares of the differences between the experimental values, $Y(t_i)$ and the predicted values $C(t_i)$; i.e.,

$$SSD = \sum_{i=1}^{n} [Y(t_i) - C(t_i)]^2$$

To obtain the theoretical breakthrough curve, the Eq. (4) is integrated numerically using a 24-term Gaussian Legendre quadrature formula (Abramowitz and Stegun, 1970). The modified Bessel function, I_0, is approximated by a Chebyshev polynomial (Abramowitz and Stegun, 1970). Eleven equally spaced points from the experimentally determined breakthrough curve were used for comparison.

The program used is iterative and may be continued until the sum of squares of errors (SSD) is as small as possible. When this point is reached, the current values of D, K_1 and K_2 are accepted as the true values.

Once the parameters D, K_1 and K_2 for a specific soil and a specific element are determined, the relative concentration (i.e., $c/c_0 = C$) is a function of z and t only. Our attempt is, however, to determine the migration rate of a particular relative concentration. The question is, knowing all the parameters (D, K_1, K_2, α, v and c_0) for a given soil and a given element, how long will it take for a particular relative concentration, C, to reach a given depth, say ground water. Mathematically, what we are asking is the following: Find a function $z = z(t)$ so that for any time, $t > 0$, the following is true:

$$C(z(t), t) = C'$$

Thus, for any time $t > 0$, $z(t)$ gives the location of the relative concentration C'. The migration rate of C' would then be given by dz/dt.

The function $C(z(t), t) = C'$ is complicated, therefore it is not possible to solve for z(t) directly. However, one can find the values of z vs. t for each c'=0.1, 0.2, ..., 0.9 by interpolation. A computer program was developed to find the steady-state migration rates of c'. Using Eq. 4, an array of c' vs. -z was calculated for 40 different times from 0.1 to up to 200 days. The spline function (Erh, 1972) was then used to calculate the value of z vs. t for each one of the c'=0.1, 0.2, ..., 0.9 giving a series of points along the curve $z = z(t)$, Figure 1. Note that in general $z = z(t)$ is not a straight line, however, for depths greater than about 10 cm, the curve becomes linear for all practical purposes. That is, it achieves a steady-state condition.

By estimating the steady-state velocity using the "linear" portion of the curve, we can determine the effect of change in the soil-leachate system on migration rates using multiple regression analysis. The main characteristics of the soils and leachates have been measured to identify the effect of soil and leachate properties on Cd, Ni, and Zn attenuation. The soil parameters are, a) percent sand, silt, and clay, and b) free iron oxides (FeO); for leachate they are a) total organic carbon (TOC), and b) total inorganic salts of Ca, Mg, Na, and K.

All the migration rates were adjusted to pore water velocity of 25 cm/day. The average pore water velocity for the experiment was about this value. It was observed, although not in all cases that when calculating the migration rates for each element by changing the pore water velocity, the migration rates for all relative concentrations would change accordingly. In other words most of the velocities follow the simple rule of being halved when the leachate velocity is halved. So we assume that the velocity of a given concentration ratio is proportional to the pore velocity of the leachate and can therefore put the Cd, Ni, or Zn velocity at a particular relative concentration C' and particular pore fluid velocity, v

$$\text{Vel}(C',v) = v(\text{A1}\cdot\text{FACTR-1} + \text{A2}\cdot\text{FACTR-2} \_ \ldots + \text{AN}\cdot\text{FACTR-N})/25 \qquad (5)$$

The factors FACTR-i, i-1, ..., N, in Eq. (5) are the particular soil leachate properties under consideration.

The application of this type of equation is of course only valid if the migration rate is proportional to the pore velocity of the carrier fluid. Otherwise multitude of additional experiments will need to be undertaken with pore velocity as an additional variable. But preliminary experiments indicate that over at least a limited range, this proportionality is maintained.

It was determined in the course of our experiments that it is the ratio of the forward and backward reaction rates which is the dominant factor in determining the breakthrough curve, as opposed to the absolute magnitude of K_1 or K_2. A plot of the values of K_1 and K_2 which give an acceptable fit of the theoretical breakthrough curve to the experimental curve results in a straight line with a slope equal to K_1/K_2. The line segments generated for each of the soils reported varied within a narrow range if at all at different fluid velocities. For example, when flux was changed fourfold (i.e., 3 ml/hr to 12 ml/hr) the K_1/K_2 ratios varied according to a common trend but to a limited extent for the soils involved (see Figure 2). Such narrow ranges of differences in slope

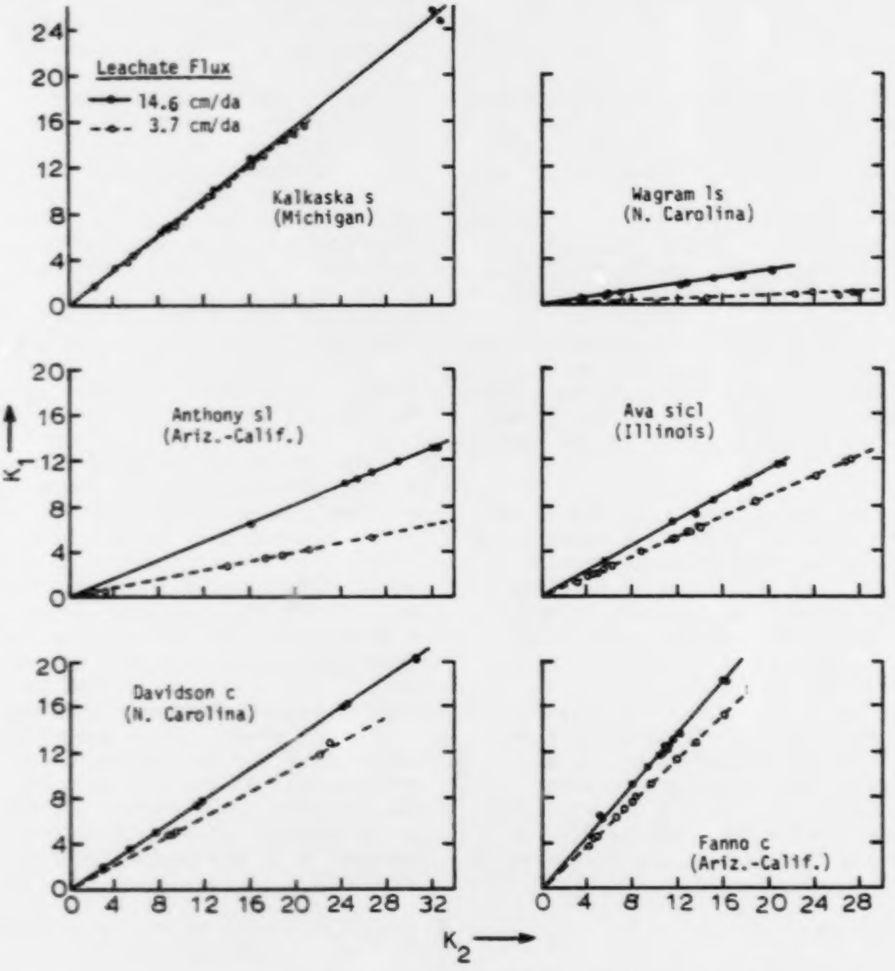


Figure 2. Line segments for six soils relating forward (K_1) and backward (K_2) reaction coefficients as influenced by flux, where: Rate of Adsorption $\partial n/\partial t = K_1 c - K_2 n$ (Eq. 2).

of line segments as a result of differences in fluid velocities are not universal for all soils. Nicholson sic and Molokai c are notable exceptions according to soils from our laboratory not reported here. Nevertheless, for the purpose of model development we chose to assume flux is of much less importance as a variable than other parameters in the soils used in this research program (Alesii et al., 1979).

The flux dependency of the diffusion coefficient also needs to be considered. A true diffusion coefficient should be independent of pore velocity (Bresler, 1973). But since the D term in the Lapidus-Amundson equation is actually a combination diffusion-dispersion term, there will be some flux dependence since the dispersion coefficient is a function of pore velocity. The diffusion coefficient has been shown to be independent of the salt concentration and dependent on only the water concentration for all practical purposes in soil-water systems (Porter et al., 1960; Kemper and van Schaik, 1966). Kemper and van Schaik (1966) propose a functional relationship between the diffusion coefficient, D, and the volumetric water content, θ, as being $D_p(\theta) = D_o a e^{b\theta}$; where a and b are empirical constants, and D_o is the diffusion coefficient in a free-water system. This relationship has been found to hold when the range of water content cooresponds to 0.30 to 15 bars suction by Olsen and Kemper (1968), when b equals 10 and a ranges from 0.001 in clays to 0.005 in sandy loams. These values for a and b were also successfully applied by Bresler (1973), and Melamed et al. (1977).

Bresler (1973) reports that many investigators have shown a linear relationship between the dispersion coefficient D_h and the average pore velocity v in the form $D_h(V) = \lambda|v|$ where λ is an empirically determined constant. Bresler (1973) reports values for λ of 0.28, 0.39, and 0.55; while Melamed et al. (1977) use a value of 0.40.

The net result is that the diffusion-dispersion term, D, is related to D_p and D_h as follows:

$$D(\theta,V) = D_p(\theta) + D_h(V) \tag{6a}$$

$$D(\theta,V) = D_o a e^{b\theta} + \lambda|V| \tag{6b}$$

In the experiments which we did, the values for v were on the order of 0.82 cm/hr in Davidson clay and 1.17 cm/hr in Wagram loamy sand. Using these flux rates and the D_o of chloride (0.04 cm^2/hr) as a reference point, it can be seen from the relation above that D_h is more than an order of magnitude greater than D_p (0.23 cm^2/he vs 0.0048 cm^2/hr in Davidson clay). In the flux range in which the experiments were run, the equation predicts that D_h describes 98% of D. By decreasing the flux by an order of magnitude, the D_h term should still describe 83% of D. We assume therefore for the purposes of model development that the relationship between the diffusion-dispersion coefficient and flux α remains linear over the range of interest. Biggar and Nielsen (1976) present a relation between the apparent diffusion coefficient, D, and pore water velocity v, $D = 0.6 + 2.93\, v^{1.11}$ with an r value of 0.795.

We regress the soil and leachate properties having most effect on migration rates with the migration rates in the following way: The regression equation is written one variable at a time with all variables available to bring into the equation at each step. The first variable in the equation is that one which does the most to explain the variation in the migration rates. The second variable to enter the equation is that one which does the most to explain the variation in the migration rates not already explained by the first variable. Variables continue to be added in this way until either all variables are in the equation or until none of the unused variables are statistically significant in explaining the remaining variation in the migration rates.

INTERPRETATION OF RESULTS

Cd - 114 cases with Ni and Zn

$$V.1 = \frac{V}{25}[32.517/CLAY + 0.27825 \times CLAY + 0.0100 \times (CLAY + SILT)^2 - 105.673/SILT + 1.3051 \times SAND + 4.5440 \times (TOC + SALT) - 97.2421]$$

$$R^2 = 0.74$$

$$V.5 = \frac{V}{25}[28.896/CLAY + 0.24376 \times CLAY + .008847 \times (CLAY + SILT)^2 - 92.1247/SILT + 1.1468 \times SAND + 4.20529 \times (TOC + SALT) - 85.6638]$$

$$R^3 = 0.73$$

$$V.9 = \frac{V}{25}[25.428/\text{CLAY} + 0.21597 \times \text{CLAY} + .007807 \times (\text{CLAY} + \text{SILT})^2 - 79.5671/\text{SILT} + 1.0046 \times \text{SAND} + 3.8101 \times (\text{TOC} + \text{SALT}) - 75.2849]$$

$$R^2 = 0.73$$

Cd - 75 cases, no Ni or Zn

$$V.1 = \frac{V}{25}[37.2697/\text{CLAY} + 9.40178/\text{FeO} - 0.0825 \times \text{SAND} + 0.017126 \times (\text{SILT} \times \text{FeO}) + 21.2165 \times \text{SALT} + 1.4111 \times \text{TOC} - 2.7050]$$

$$R^2 = 0.82$$

$$V.5 = \frac{V}{25}[35.3135/\text{CLAY} + 8.0903\ /\text{FeO} - 0.08001 \times \text{SAND} + 0.01496 \times (\text{SILT} \times \text{FeO}) + 18.7552 \times \text{SALT} + 1.47171 \times \text{TOC} - 2.0804]$$

$$R^2 = 0.82$$

$$V.9 = \frac{V}{25}[33.3546/\text{CLAY} + 6.9232\ /\text{FeO} - 0.076324 \times \text{SAND} + 0.013806 \times (\text{SILT} \times \text{FeO}) + 16.01493 \times \text{SALT} + 1.40034 \times \text{TOC} - 1.52744]$$

$$R^2 = 0.81$$

Ni - 72 cases with Cd and Zn

$$V.1 = \frac{V}{25}[115.0336/\text{CLAY} + 0.14880 \times \text{CLAY} - 82.4514/\text{SILT} + 0.000966 \times \text{SAND}^2 - 6.9386\ /\text{FeO} + 4.3635 \times \text{TOC} - 3.5346]$$

$$R^2 = 0.81$$

$$V.5 = \frac{V}{25}[92.7205/\text{CLAY} + 0.12965 \times \text{CLAY} - 66.9761/\text{SILT} + 0.0008 \times \text{SAND}^2 - 5.4369/\text{FeO} + 4.1174 \times \text{TOC} - 3.0682]$$

$$R^2 = 0.81$$

Ni - 72 cases with Cd and Zn (contd)

$$V.9 = \frac{V}{25}[80.5799/\text{CLAY} + 0.11377 \times \text{CLAY} - 57.5043/\text{SILT} + 0.00068 \times \text{SAND}^2 - 4.6977/\text{FeO} + 3.8282 \times \text{TOC} - 2.7105]$$

$$R^2 = 0.77$$

Ni - 44 cases, no Cd or Zn

$$V.1 = \frac{V}{25}[-1.9665 \times \text{SAND} - 0.04175 \times (\text{CLAY} \times \text{SAND}) - 0.07765 \times (\text{CLAY} \times \text{SILT})\ 0.00771 \times \text{SILT}^2 + 52.8340 \times \text{SALT} - 164.7779 \times \text{SALT}^2 + 200.472]$$

$$R^2 = 0.89$$

$$V.5 = \frac{V}{25}[-1.60976 \times \text{SAND} - 0.03404 \times (\text{CLAY} \times \text{SAND}) - 0.06332\ (\text{CLAY} \times \text{SILT}) - 0.006397 \times \text{SILT}^2 + 44.1637 - 135.41869 \times \text{SALT}^2 + 163.9379]$$

$$R^2 = 0.87$$

$$V.9 = \frac{V}{25}[-1.3083 \times \text{SAND} - 0.02824 \times (\text{CLAY} \times \text{SAND}) - 0.05098 \times (\text{CLAY} \times \text{SILT}) - 0.005567 \times \text{SILT}^2 + 49.5652 \times \text{SALT} - 156.0114 \times \text{SALT}^2 + 133.0813]$$

$$R^2 = 0.78$$

Zn - 29 cases, no Cd or Ni

$$V.1 = \frac{V}{25}[-0.96122 \times \text{CLAY} + 0.011347 \times \text{CLAY}^2 + 0.4278 \times (\text{CLAY} + \text{SILT}) - 0.002640 \times (\text{CLAY} + \text{SILT})^2 + 31.1308 \times \text{TOC}^2 + 11.9237 \times \text{SALT} + 1.4004]$$

$$R^2 = 0.75$$

$$V.5 = \frac{V}{25}[-0.8990 \times \text{CLAY} + 0.010598 \times \text{CLAY}^2 + 0.4109 \times (\text{CLAY} + \text{SILT}) - 0.00255 \times (\text{CLAY} + \text{SILT})^2 + 28.47561 \times \text{TOC}^2 + 10.8695 \times \text{SALT} + 0.9522]$$

$$R^2 = 0.75$$

$$V.9 = \frac{V}{25}[-0.89588 \times \text{CLAY} + 0.010568 \times \text{CLAY}^2 + 0.4225 \times (\text{CLAY} + \text{SILT}) - 0.002644 \times (\text{CLAY} + \text{SILT})^2 + 25.8125 \times \text{TOC}^2 + 9.7207 \times \text{SALT} + 0.65902]$$

$$R^2 = 0.73$$

Zn - 54 cases with Cd and Ni

$$V.1 = \frac{V}{25}[14.6428/\text{CLAY} - 0.14959 \times \text{CLAY} - 23.3821/\text{SILT} + .0045 \times (\text{CLAY} \times \text{FeO}) - 0.0035519 \times (\text{SAND} \times \text{SILT}) + 1.4833 \times \text{TOC} + 8.1533]$$

$$R^2 = 0.63$$

Zn - 54 cases with Cd and Ni (contd)

$$V.5 = \frac{V}{25}[13.7075/\text{CLAY} - 0.11745 \times \text{CLAY} - 19.824/\text{SILT} + 0.003747 \times (\text{CLAY} \times \text{FeO}) - 0.002812 \times (\text{SAND} \times \text{SILT}) + 0.76496 \times \text{TOC} + 6.5722]$$

$$R^2 = 0.62$$

$$V.9 = \frac{V}{25}[13.1353/\text{CLAY} - 0.09602 \times \text{CLAY} - 17.8912/\text{SILT} + 0.003123 \times (\text{CLAY} \times \text{FeO}) - 0.002267 \times (\text{SAND} \times \text{SILT}) + 0.4699 \times \text{TOC} + 5.5240]$$

$$R^2 = 0.61$$

To use these equations:

1) Estimate Clay, Silt, & Sand (%)
2) Estimate TOC of leachate (%)
3) Estimate total ion content of the

leachate (%): This is the sum of soluble salts and iron in solution.

4) Estimate free iron oxide content (%).
5) Estimate the pore velocity of the leachate (cm/day). (The Darcian velocity divided by the leachate filled porosity.)
6) Determine the particular relative concentration.
7) Substitute the quantities from steps 1-5 into the equation determined from step 6.

For example, suppose the soil has the characteristics:

Clay content = 15%, silt content = 20%, free iron oxide content - 1.5%. Suppose the leachate has total soluble ions 0.08%. If the porosity of the soil was 0.38 and the infiltration rate was 0.6 $cm^3/cm^2/day$, then the pore velocity would be 0.6/.38=1.6 cm/day. Suppose the initial cadmium concentration in the leachate is 2 ppm and the concentration limit was 1 ppm. Then the relative concentration of interest is 0.5. Substitution into the equation for V.5 yields

$$
\begin{aligned}
V.5 = \frac{1.6}{25}[&35.31/(15) \pm 8.09/(1.5) - \\
&.08(65) + .015(20 \times 1.5) + \\
&18.76(.08) + 1.47 \times TOC(1.1) \\
&- 2.08] \\
= {} &0.258 \text{ cm/day Alone and } 0.291 \text{ mixed}
\end{aligned}
$$

To summarize this point, we have plotted the data from all the columns run and have matched theoretical curves to the observed curves to get individual values for D, K_1 and K_2 for each column. At this point the only data that have been used are values of α, v, c_0 and the experimental breakthrough curve from the column. And for selected relative concentrations we have migration rates for each column.

To generalize these results from the few columns run to a more general setting and also to display the results in an easily accessible form we make use of multiple regression equations. One regression equation for each of the selected relative concentrations.

Data in Table 1 showing R^2 values were assembled to show that nearly all of the variables influencing attenuation were identified. For the most part, 77-90%; 73-

TABLE 1. COMPARISON OF CORRELATION COEFFICIENTS OF VELOCITY (MIGRATION RATE) THROUGH SOIL OF Cd, Ni, and Zn ALONE AND MIXED IN LANDFILL-TYPE LEACHATES

	Ni		Cd		Zn	
Velocity	Ni alone	Ni + Cd + Zn	Cd alone	Cd + Ni + Zn	Zn alone	Ni + Cd + Zn
	R^2	R^2	R^2	R^2	R^2	R^2
V.1	0.8941	0.8115	0.8249	0.7377	0.7512	0.6350
V.2	0.8895	0.8120	0.8222	0.7355	0.7534	0.6286
V.3	0.8909	0.8137	0.8227	0.7354	0.7526	0.6252
V.4	0.8749	0.8092	0.8173	0.7323	0.7521	0.6199
V.5	0.8684	0.8081	0.8218	0.7348	0.7504	0.6164
V.6	0.8570	0.8051	0.8196	0.7329	0.7492	0.6131
V.7	0.8457	0.8014	0.8170	0.7314	0.7429	0.6132
V.8	0.8231	0.7914	0.8144	0.7306	0.7374	0.6129
V.9	0.7813	0.7743	0.8125	0.7274	0.7259	0.6081

83%; and 60-75% of the total variation for Cd, Ni and Zn, respectively, are described by the combined influence of independent variables. Considering the great number of soil and leachate variables, this unexpectedly high achievement is fortunate and lends confidence in this approach to evaluating metal attenuation by soil.

The velocities of Zn through soil tended to be about the same whether contained singly or in mixed combination in landfill-type leachates at concentrations up to 100 ppm of each metal. Velocities of Cd were not significantly influenced by Zn but were significantly influenced by Ni at the 5% level.

Velocities of Ni, on the other hand, were not significantly influenced by Cd but were influenced at the 5% level by Zn. In view of the lack of significance in four out of six comparisons and the low level of significance (0.05) in the other two comparisons, it appears that attenuation is not appreciably influenced by the presence of these metals in mixed combinations at concentrations up to 100 ppm of each in the leachates. These findings might appear to contradict the results reported for the effects of common salts in leachates. The apparent discrepancy is resolved by virtue of the fact the common salts in the leachates were compared at much higher levels of concentration than were provided for Cd, Ni, or Zn. Also we have a limited number of cases for the Cd, Ni, and Zn compared with those of common salts. For example, the velocity of Cd was found to increase through a given soil from 0.345, 0.411 to 0.462 cm/day as the salt content of a landfill-type leachate increased from 0.02, 0.05, to 0.08%.

These equations also provide quantitative data demonstrating the comparative migration rates of Cd, Ni, and Zn under a variety of environmental conditions. At V.5, for example, by using the above soil the relative rates of migration when the metals are present singly in the solid waste leachates were 0.462, 0.258, and 0.117 cm/day for Ni, Cd, and Zn, respectively. When all three metals are present together, the rate of movement of Ni, Cd, and Zn are 0.442, 0.291, and 0.128 cm/day, respectively.

LIMITATIONS AND ADVANTAGES OF THE LAPIDUS-AMUNDSON MODEL APPROACH

Limitations: Caution must be exercised when using this approximation for several reasons. First, these were based on column experiments and not field conditions. Second, although the regression of velocity with both soil and leachate properties have an R^2 value of high order, considerable variation in the actual velocity values and those predicted by the regression equations are still present. Here we feel that caution should be exercised when these regression equations are required for highly accurate predictions of metal movement. Rather they should be used to gain some idea of the degree to which the selected soil and leachate properties either contribute to or detract from metal transport velocity.

Refinements in the Model are needed ir order of most increase in predictive capability per expenditure of a given amount of development work. These include:

1) Tests with leachates radically different from those used to date.
2) More analyses of sensitivity of output to character of input so it can be determined where to exercise most care in collecting input data and which experimental conditions to control most closely in developing the Model, such as:
    - --importance of soil bulk density and pore size distribution.
    - --nature of total organic carbon.
    - --identification of the effect of other hydrous oxides such as Mn and Al.
    - --importance of soil-leachate matrix pH.

Advantages: The Model provides certain advantages over others:

1) Less complicated than many other models.
2) Does not require infinite information of attenuation mechanisms which would need many years to discover and evaluate.
3) D, K_1, and K_2 have been derived as real values from research experimental data making it possible to apply the Model to actual landfill disposal problems for attenuation of poten-

tially hazardous metals. In short, D, K_1, and K_2 represent real values beyond armchair theory.

4) The Model is most likely to be applied in its present form to the evaluation of disposal sites because it is

   --independent of computers, as far as the ultimate user is concerned.

   --much easier to use the products in the form of mathematical equations or tables,

   --less demanding for data than other prominent simulation model approaches,

   --no more limited by the quality of input data than other approaches, and (for a given site) much less limited by quantity of input data than other approaches,

   --most likely to be used in evaluating relative migration of a single metal at several alternative sites (because of extrapolation problems, no claim of predicting exact movement rate in undisturbed soil is made. However, the Model is very likely to estimate accurately metal movement rate in disturbed soils as might be found when landfills are lined with clay-soil mixtures or with native soils).

5) Concerned with nonconservative solutes (such as metals) and nonconventional leachates as well as raw, unspiked municipal solid waste leachates.

6) Not conflicting with the large hydrology modeling programs of the USGS.

7) Conveniently and accurately related to easily measurable physical and chemical properties of the soil-leachate system.

ACKNOWLEDGMENTS

This research was supported in part by the U.S. Environmental Protection Agency, Solid and Hazardous Waste Research Division, Municipal Environmental Research Laboratory, Cincinnati, OH. Grant No. R 805731-01 and the University of Arizona, Soils, Water and Engineering Department. Arizona Agricultural Experiment Station Paper No.

The authors wish to thank Rodney Campbell and Dan O'Donnell for assistance during the initial phases of the modeling program and Bruno Alesii and Nic Korte in the development of some of the Cd migration data.

REFERENCES

1. Abramowitz, M., and I.A. Stegun, eds. 1970. Handbook of mathematical functions. Ninth Printing. U.S. Department of Commerce. National Bureau of Standards. Applied Mathematics Series 55, pp. 916, 378.

2. Alesii B.A., W.H. Fuller, and M.V. Boyle. 1979. Effect of leachate flow rate on metal migration through soil. Az. Agr. Expt. Sta. (in press).

3. Alloway, W.H. 1968. Agronomic controls over the environmental cycling of trace elements. Adv. Agron 120:257-274.

4. Biggar, J.W., and D. Nielsen. 1976. Spatial variability of the leaching characteristics of a field soil. Water Resources Res. 12:78-84.

5. Black, C.A. (ed.) 1965. Methods of soil Analysis. Part 2. Chemical and microbial properties. Agron. Monogr. No. 9. Am. Soc. Agron., Madison, WI.

6. Bresler, Eshel. 1973. Simultaneous transport of solutes and water under transient unsaturated flow conditions. Water Resources Res. 9:(4).

7. Davidon, W.C. 1959. Variable metric method of minimization. ANL-5990 (Aragonne National Lab. U.S. AEC Research and Develop. Rep.)

8. Davidson, J.M., D.R. Baker, and G.H. Brusewitz. 1975. Simultaneous transport of water and adsorbed soilutes through soil under transient flow conditions. Amer. Soc. Agr. Engr. Transactions. 18:535-537.

9. Fuller, W.H. 1978. Investigation of landfill leachate pollution attenuation by soils. EPA-600/2-78-158. U.S. Environmental Protection Agency, Cincinnati, OH.

10. Fuller, W.H. 1977. Movement of selected metals, asbestos, and cyanide in soil: Application to waste disposal problems, 1977. Environ. Protec. Tech. Ser. EPA-600/2-77-220. U.S. EPA, Cincinnati, OH 45268.

11. Jenne, E.A. 1968. Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: The significant role of hydrous Mn and Fe oxides. Adv. Chem. Ser. 73:337-387.

12. Kemper, W.D. and J.C. van Schaik. 1966. Diffusion of salts in clay-water systems, Soil Sci. Soc. Amer. Proc. 30: 534-540.

13. Korte, N.E., J. Skopp, W.H. Fuller, E. E. Niebla, and B.A. Alesii. 1976. Trace element movement in soil : Influence of soil physical and chemical properties. Soil Sci. 122:350-359.

14. Korte, N.E., J. Skopp, E.E. Niebla, and W.H. Fuller. 1975. A baseline study on trace metal elution from diverse soil types. Water, Air. Soil Pollut. 5:149-156.

15. Lapidus, L. and N.R. Amundson. 1952. Mathematics of absorption in beds. VI. The effect of longitudinal diffusion in ion exchange and chromatographic columns. J. Phys. Chem. 56: 984-988.

16. Leeper, G.W. 1978. Managing the heavy metals on land. Marcel Dekker, Inc. New York. 121 pp.

17. Lisk, D.J. 1972. Trace metals in soils, plants, and animals. Adv. Agron. 24:267-325.

18. Melamed, D., R.J. Hanks, and L.S. Willardson. 1977. Model of salt flow in soil with a source-sink term. Soil Sci. Soc. Amer. J. 41:29-33.

19. Nielsen, D., and J.W. Biggar. 1962. Miscible displacement: III. Theoretical considerations. Soil Sci. Soc. Am. Proc. 26:216-221.

20. O'Donnell, D.F., B.A. Alesii, J. Artiola-Fortuny and W.H. Fuller. 1977. Predicting cadmium movement through soil as influenced by leachate properties. U.S. EPA Report (in press).

21. Olsen, S.R. and W.D. Kemper. 1968. Movement of nutrients to plant roots. Advan. Agron. 30:91-151.

22. Porter, L.K., W.D. Kemper, R.D. Jackson, and B.A. Stewart. 1960. Chloride diffusion in soils as influenced by moisture content. Soil Sci. Soc. Amer. Proc. 24:460-463.

23. Selim, H.M., J.M. Davidson, and R.S. Mansell. 1976. Evaluation of a two-site absorption-desorption model for describing solute transport in soils. Summer computer simulation conference.

24. Selim, H.M., and R.S. Mansell. 1976. Analytical solution of the equation for transport of reactive solutes through soils. Water Resources Research 12:528-532.

25. Skopp, J., and A.W. Warrick. 1974. A two-phase model for miscible displacement of reactive solutes in soils. Soil Sci. Soc. Am. Proc. 38: 545-550.

26. USDA. 1954. Saline and alkali soils. Agri. Handbook #60. U.S. Govt. Print. Office, Wash. D.C.

27. Van Genuchten, M.T. 1978. Simulation models and their application to landfill disposal siting; A review of current technology. In Land Disposal of Hazardous Wastes. Proc. 4th Ann. Res. Symp. Ed. D.W. Shultz. EPA-600/9-78-016. U.S. Environmental Protection Agency, MERL, Cincinnati, OH. 425 pp.

28. Van Genuchten, M.T., and P.J. Wierenga. 1976. Mass transfer studies in sorbing porous media: I. Analytical solutions. Soil Sci. Soc. Amer. J. 40:473-480.

ALSO

Fuller, W.H., A. Amoozegar-Fard and G.E. Carter. 1979. Predicting movement of selected metals in soils: Application to disposal problems. Proc. Fourth Ann. Res. Symp., San Antonio, TX, March 1978. U.S. Environ. Protect. Agency. EPA-600/9-79-023a. Cincinnati, OH 45268. pp 358-374

Erh, K.T. 1972. Application of the spline function to soil science. Soil Sci. 114: 333-338.

AQUEOUS CHEMISTRY AND ADSORPTION OF HEXACHLOROCYCLOPENTADIENE BY EARTH MATERIALS

Sheng-Fu J. Chou, Barry W. Fisher, and Robert A. Griffin
Illinois State Geological Survey
Champaign, IL 61820

ABSTRACT

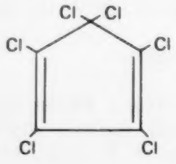
The aqueous chemistry, adsorption, and mobility of hexachlorocyclopentadiene (C-56) in soil materials were studied in the laboratory. The solubility of C-56 in waters, soil extracts, and sanitary landfill leachates ranged from 1.03 to 1.25 ppm. Sodium hydroxide and sodium chloride decreased the solubility of C-56 in water; sodium hypochloride slightly increased its solubility. C-56 underwent rapid hydrolysis at pH 2.51 and slower hydrolysis at pH 8.45 and 11.73. When exposed to sunlight, the half-life of C-56 was less than 4 min in aqueous solution and less than 1.2 min in hexane solution. At least four products of hydrolysis and photolysis were identified. Hexachlorocyclopentenone was the major product in low pH water, and the diolefins *cis*- and *trans*-pentachlorobutadiene were the major products in mineralized water or high pH water.

Freundlich adsorption isotherm plots of C-56 sorption on soils and clay minerals yielded linear regression lines with coefficients of correlation (r^2) of at least 0.98. C-56 was found to be readily adsorbed by the soil materials. The adsorption capacity and mobility of C-56 were highly correlated with the total organic carbon (TOC) content of nine soil materials ($r^2 = 0.99$) and appear to be predictable from the TOC content of soils. A further conclusion was that products of the degradation of C-56 appear to migrate through soils and might cause more of a problem than C-56 itself.

INTRODUCTION

Hexachlorocyclopentadiene (C-56 or "hex" waste) is a highly toxic compound that poses a potential occupational hazard (Hoecker et al., 1977). Fathead minnows were adversely affected at concentrations of C-56 as low as 3.7 ppb, and significant decreases in survival occurred at 7.3 ppb (Spehar et al., 1979). Because C-56 occurs as a by-product from production of chemical feed stocks, pesticides, adhesives, resins, and other related products, large quantities are produced in the United States each year. Even with governmental bans on the use of certain chlorinated pesticides, there is currently no documentation that the production of C-56 has subsided. The reason may be that C-56 is commercially important as a chemical intermediate, although it has no end uses of its own (Bell, Ewing, and Lutz, 1978, and National Academy of Sciences, 1978).

C-56 is a light yellow liquid. It is extremely volatile and photoreactive in sunlight with near-surface half-lives of less than 10 min in aquatic systems (Zepp et al., 1979). The empirical formula of C-56 is C_5Cl_6 and its structure formula is:



The present environmental concern is the disposal of large quantities of C-56 that is produced annually as a by-product of pesticide and other manufacturing processes. Therefore, the study of C-56 waste has broad application to many industries. The limited amount of information presently available indicates that C-56 has a fairly strong affinity for soil. The mechanisms of attenuation in soil materials are unknown. Data on the factors affecting C-56 attenuation by soil materials, its solubility in waters and landfill leachates, and its mobility in soils would provide a useful basis for determining waste treatment methods, for predicting C-56 migration under landfills, and for selecting and designing future disposal sites.

The specific objectives of this study were to determine the attenuation mechanisms and capacity of selected earth materials for C-56, to determine the effects of caustic soda-brine on the attenuation and solubility of C-56, to develop a chemical model to predict C-56 migration through soil materials, and to identify the major degradation products of C-56 in the environment.

This is a report of work conducted as part of Grant No. R806335-010 from the U.S. Environmental Protection Agency, Cincinnati, Ohio. The results should be considered preliminary and subject to reinterpretation if future results require it. Mention of trade names does not constitute endorsement.

CURRENT RESEARCH MATERIALS AND METHODS

Reagents

Reagent grade C-56 was obtained from Pfaltz and Bauer, Inc., Stamford, CT, and was used without further purification. An analytical standard of C-56 (lot #0213) was obtained from U.S. EPA, Research Triangle Park, NC. Both materials were identical and the purity was approximately 98%. Analytical reagent grade sodium hydroxide, sodium chloride, and sodium hypochloride were used in the solubility studies.

Waters and Leachates

Distilled water, deionized water, tap water, Sugar Creek water, soil extracts (soil : tap water = 1 : 3), Blackwell landfill leachate, and Du Page landfill leachate were selected for use in the solubility study. Leachates were centrifuged through a continuous flow centrifugation apparatus (Model JCF-Z, Beckman Instruments) at approximately 17,000 rpm, prior to passing through a 0.22 μm pore size Millipore® cellulose acetate membrane. Tap water, deionized water, Sugar Creek water, and soil extracts were also passed through 0.22 μm membrane before use.

Adsorbents

Earth materials, representing a wide range in characteristics, were selected as adsorbents. They were: Ca-montmorillonite, Ca-bentonite, illite, kaolinite, silica sand, and five soils: Houghton muck, Catlin sil, Flanagan sicl, Bloomfield ls, and Ava sicl.

Solubility Studies

In the solubility studies, 350 mL of water, soil extract, or landfill leachate were placed into 500-mL amber glass bottles. C-56 (0.5 mL) was added to each bottle, and the bottle was capped with a teflon-lined cap. The water and C-56 mixtures were shaken in a constant temperature water bath (22° ± 1°C) at moderate speed for 15 hours and then left quiescent for 3 hours. Aliquots of the aqueous solutions were centrifuged in a constant temperature centrifuge (Beckman Model J-21B at 22° ± 1°C) at 17,000 rpm for 30 min; then 5-mL aliquots of the supernatant were carefully withdrawn and placed in 15-mL screw-capped vials. All samples were extracted for C-56 three times with 5-, 5-, and 5-mL portions of water-saturated hexane. Each extraction was vibrated on a vortex mixer at fast speed for 1 min; the hexane extract was then transferred to a graduated test tube using a Pasteur pipette. Studies proved that a shaking time of 12 hours was sufficient to reach equilibrium conditions. Therefore, all solubility studies were shaken overnight (15 hours) to ensure equilibrium and for convenience. Results of preliminary studies showed that the extraction technique used in this study was much better than conventional separatory funnel extraction. The extraction efficiency was 95% or better in samples spiked with C-56 at three different concentrations. The extracts were then analyzed on a Hewlett-Packard (HP 5840A) gas chromatograph or a Perkin-Elmer Sigma I gas chromatograph (GC). Tribromobenzene was used as the internal standard. Both gas chromatographs were equipped with Ni^{63} electron capture detectors. A glass capillary column was used to facilitate the separation of the hydrolysis products of C-56 from "pure" C-56 in distilled water

TABLE 1. CONDITIONS FOR GAS CHROMATOGRAPHIC ANALYSIS

Conditions	HP 5840A and P-E Sigma I GC	Sigma I GC
Column:	6 ft x 2 mm I.D. glass column, 5% OV-17 on 100/120 mesh chromosorb WHP	28 m x 0.25 mm I.D. grade AA glass capillary column (SE-30), split ratio: 100 : 1
Injector temperature:	250°C	250°C
Column temperature:	150°C	145°C
Detector temperature:	300°C	280°C
Carrier gas:	methane/argon, flow 32 mL/min	methane/argon, velocity: 28 cm/sec

and deionized water extracts. The conditions for the gas chromatographic analysis for C-56 are shown in Table 1.

To determine the effect of caustic soda-brines and soluble salts on the aqueous solubility of C-56, several concentrations of soluble salts were added to water and the changes in solubility of C-56 were measured. The concentrations and salts used were: 0.513, 1.026, 1.465, and 2.051 M NaCl; 0.135, 0.270, 0.405, and 0.541 M NaOCl; and 0.188, 0.375, 0.563, and 0.750 M NaOH.

Identification of Degradation Products During Hydrolysis and Photolysis

In the hydrolysis study, the pH of tap water (8.45) was adjusted to 2.51, 5.80, and 11.73. Mixtures of C-56 and water were shaken in a constant-temperature water bath (22° ± 1°C) for 18 hours and then allowed to sit quiescent for at least 3 hours. Fifty-mL aliquots of the C-56 water solutions were filtered through 0.22 µm Millipore® cellulose acetate membranes. The membrances were presaturated with C-56 by soaking the membranes in C-56 saturated water prior to filtration. The membranes were then washed with deionized water and 200 mL of the C-56 saturated tap water was flushed through the membrane.

In a separate study, 50 mL aliquots of the filtered aqueous C-56 were placed in 125-mL amber serum bottles and sealed with teflon-faced septum and aluminum seals. All samples were kept in darkness and two replicate samples were analyzed at 0, 1, 2, 4, 7, and 11 days. The extraction was accomplished by placing 10-mL aliquots of the filtrates into 15-mL vials and then extracting as previously described.

In the photolysis study, 10-mL aliquots of the filtrate were placed into 15-mL vials and exposed to sunlight for 1, 3, 6, 12, and 22 min. The sunlight intensity was measured by using a YSI-Kettoring Model 65A Radiometer (Yellow Springs Instrument Co., Inc., Yellow Springs, OH). The average sunlight intensity was 770 joules-sec/m^2 (or watts/m^2). Samples were set in darkness for a few minutes and then extracted as previously described. In a separate study, 5 mL of C-56 (2 ppm) in hexane were placed in 15-mL vials and capped with teflon-lined caps, then exposed to sunlight for 0, 1, 2, 4, and 6 min. The extracts and hexane soluble C-56 were analyzed by gas chromatography. The half-life and dissipation rate were also calculated. The major hydrolysis and photolysis products were identified by mass spectrometry using a Hewlett-Packard 5985 GC mass-spectrometer and data system.

Adsorption Studies

Adsorption studies were carried out

by shaking known volumes of C-56 solution with varying weights of soil materials at a constant temperature of 22° ± 1°C in amber glass serum bottles. Amber glass was used to prevent photolysis of the C-56, and the bottles were sealed with a teflon-faced septum and an aluminum crimp-cap to prevent volatilization. The rate of adsorption of C-56 by soil materials was relatively rapid. A study indicated a shaking time of 2 hours was sufficient to reach constant concentrations of C-56 in solution. Therefore, all samples were shaken 4 hours to ensure equilibrium. The bottles were removed from the shaker and placed directly into a Model JS-7.5 rotor and centrifuged at a constant temperature of 22° ± 1°C in a Beckman Model J-21B centrifuge for 15 min at 4000 rpm. The seals were then broken and 10-mL aliquots of the clear supernatants were pipetted for C-56 analysis.

Blanks were carried through all experiments to determine the degree of adsorption of C-56 onto the surface of the bottles. The amount of adsorption was determined from the difference between the initial concentration and the equilibrium concentration multiplied by the volume of solution. A blank was subtracted, and the amount adsorbed by each test material was computed on a unit basis by dividing by the dry weight of the adsorbent.

Mobility Studies: Determination by Soil TLC and Soil Column Leaching

The method used to prepare soil TLC plates has been reported previously by Griffin and his co-workers (1977). In these studies, the C-56 was spotted 2 cm from the base and leached 10.5 cm with tap water, caustic soda-brine solution, landfill leachate, acetone/water (1 : 1), methanol, acetone, or dioxane. The plates were immersed in 0.5 cm of the respective solvent in a closed glass chamber and were removed when the wetting front reached the 10.5 cm line. The soil plates were removed and the soil was immediately scraped off in 1 cm increments, starting 1.5 cm above the base of the plate. The soils were placed in glass test tubes and extracted with hexane or other suitable organic solvents. The concentration of C-56 in the extracts was measured by GC analysis. In a soil column leaching study, a sample of Bloomfield loamy sand that had been heavily spiked with C-56 to simulate a C-56 spill was leached with 192 in. of tap water (approximately 5 to 6 times the average annual rainfall in Illinois).

RESULTS AND DISCUSSION

Solubility of C-56 in Waters and Leachates

The solubility of C-56 in tap water, Sugar Creek water, soil extracts, and landfill leachates varied from 1.03 in Sugar Creek water to 1.25 ppm in Du Page landfill leachate. The results are shown in Table 2. An increase in total organic carbon content in the test waters and leachates slightly increased the solubility of C-56. The solubility of C-56 in water has previously been reported as about 0.8 ppm (Liu et al., 1975), 1.8 ppm (Zepp et al., 1979), and 2 ppm (Atallah, Whitacre, and Butz, 1980).

An experiment showed that C-56 was not stable in distilled water or deionized water. This experiment was repeated several times. In all cases a degradation product was formed that had a retention time almost identical with that of the parent C-56. A possible explanation of this phenomenon could be the dissociation of a chlorine ion from C-56 to make the water acidic, which in turn could initiate a hydrolysis reaction. This may occur to a greater extent in purified water than in tap water because distilled water and deionized water have no buffering capacity to neutralize the acid. A similar degradation product was also observed when the pH of tap water was adjusted to values below 6.0. Representative capillary column GC chromatograms of tap water and deionized water-soluble C-56 are shown in Figure 1. GC peaks for the degradation product and for C-56 were resolved on a capillary column (Fig. 1A). There is a possibility that previous workers using a packed GC column may have measured the degradation product or a combination of the degradation product and C-56 rather than "pure" C-56. This may have led to the conclusion that greater concentrations of C-56 were present in the water samples than actually was the case.

The effect of several soluble salts on the solubility of C-56 were treated by fitting the solubility data to the Setschenow equation (1892):

$$\log \frac{S_o}{S} = Km$$

TABLE 2. SOLUBILITY OF C-56 at 22°C AFTER 15 HOURS EQUILIBRIUM IN WATERS AND LANDFILL LEACHATES USING CENTRIFUGATION TECHNIQUE

Waters and leachates	Concentration (mg/L)*
Tap water	1.08
Sugar Creek water	1.03
Bloomfield soil extract (soil : tap water = 1 : 3)	1.06
Catlin soil extract (soil : tap water = 1 : 3)	1.20
Blackwell leachate	1.19
Du Page leachate	1.25

*Each value is a mean of 2 replicates except tap water which is 20 replicates.

TABLE 3. EFFECT OF DISSOLVED SALTS ON THE WATER SOLUBILITY OF C-56 AT 22°C AND SETSCHENOW PARAMETER FOR C-56

	Setschenow parameter			
Salts	K	r^2	m (mole/L)	S_o/S
NaOH	+0.266	0.996	0.188	1.099
			0.375	1.239
			0.563	1.396
			0.750	1.563
NaCl	+0.161	0.970	0.513	1.306
			1.026	1.622
			1.465	1.683
			2.051	2.239
NaOCl	-0.058	0.889	0.135	0.998
			0.270	0.956
			0.405	0.942
			0.541	0.940

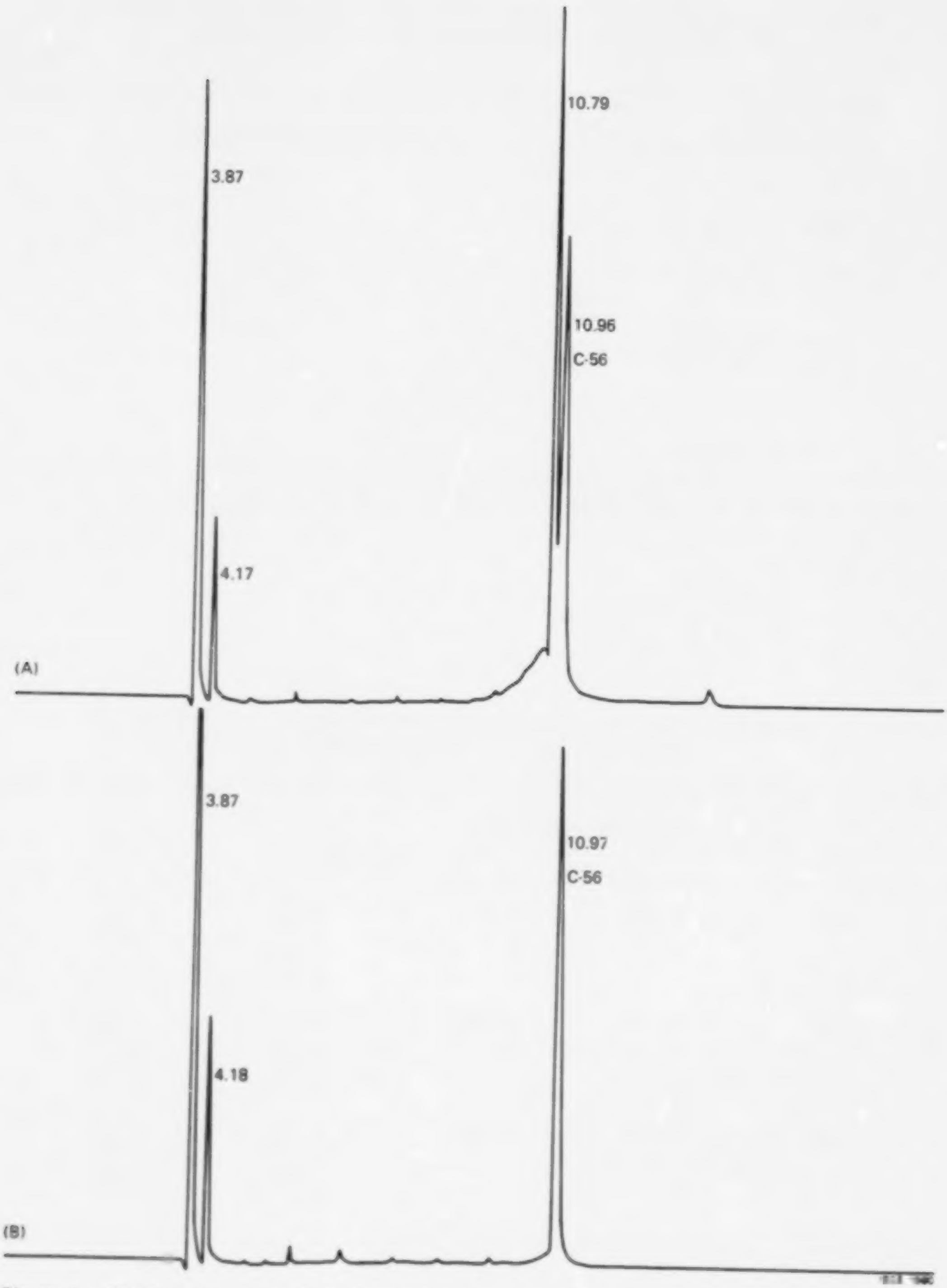


Figure 1. GC chromatograms: (A) Deionized water soluble C-56, and (B) Tap water soluble C-56 (28 m x 0.22 mm glass capillary column).

The results are given in Table 3; listed are the observed solubility ratios, S_o/S where S_o is the solubility (ppm) of C-56 in tap water and S its solubility (ppm) in a salt solution of concentration m (mole/L). Table 3 also gives the Setschenow parameter, K. The best values of K were determined by linear regression analysis of $\log \frac{S_o}{S}$ as a function of m; the coefficient of correlation (r^2) is also given in the table.

Of the three salts studied, sodium hydroxide and sodium chloride decrease the solubility of C-56 in water (K = +) and sodium hypochloride slightly increases its solubility (K = -). A similar effect of sodium chloride on water solubility of lindane was reported elsewhere (Masterton and Lee, 1972).

Hydrolysis and Photolysis

C-56 undergoes rapid hydrolysis at pH 2.51 and slower hydrolysis at pH 8.45 and 11.73. In a preliminary study, we found that C-56 is not stable in either distilled water or deionized water. In this study, we affirmed that low pH causes hydrolysis. Figures 2A and 2B show gas chromatograms obtained by using a packed GC column. Peaks c, d, and the combined peak for the hydrolysis product and C-56 decreased as the pH of tap water was increased. However, the height of peaks a and b (see Figures 2A-D) were slightly increased as the pH was increased. Yu and Atallah (1977) found C-56 was hydrolyzed much faster at pH 12 than at 3 and 6. We have repeated this experiment several times, and it appears that the large peak close to the C-56 peak was the major hydrolysis product at low pH, but that it cannot be resolved into a distinct peak using a packed GC column as is illustrated in Figure 2.

In the photolysis study, we found peaks c and d (see Figure 2A) were also the major degradation products. Of interest was the height of peak d which increased in tap water when the photolysis time was increased. However, peak d remained constant in hexane soluble C-56 solutions exposed to light.

Values of the first-order rate constant (K), the half-life ($t_{1/2}$), and regression coefficient (r^2) for the dissipation of C-56 in solutions exposed to sunlight are given in Table 4. The dissipation rate of C-56 in aqueous solution and hexane follows a first-order reaction. C-56 dissipated much faster in hexane than in tap water. These results also show that C-56 was dissipated in a closed vial when it was exposed under sunlight; this indicates that the dissipation of C-56 under the tested conditions was mainly due to photolysis and/or hydrolysis and was only partially due to volatilization.

TABLE 4. FIRST-ORDER RATE CONSTANT (K), HALF-LIFE ($t_{1/2}$), AND REGRESSION COEFFICIENT (r^2) FOR THE DISSIPATION OF C-56 IN TAP WATER AND HEXANE UNDER SUNLIGHT AND DARKNESS

Treatment	K	$t_{1/2}$	r^2
Under sunlight			
C-56 hexane in capped vial	0.58 min^{-1}	1.19 min	0.9996
C-56 water in capped vial	0.19 min^{-1}	3.71 min	0.9972
Under darkness			
C-56 water in sealed bottle	0.04 day^{-1}	16.09 day	0.9243

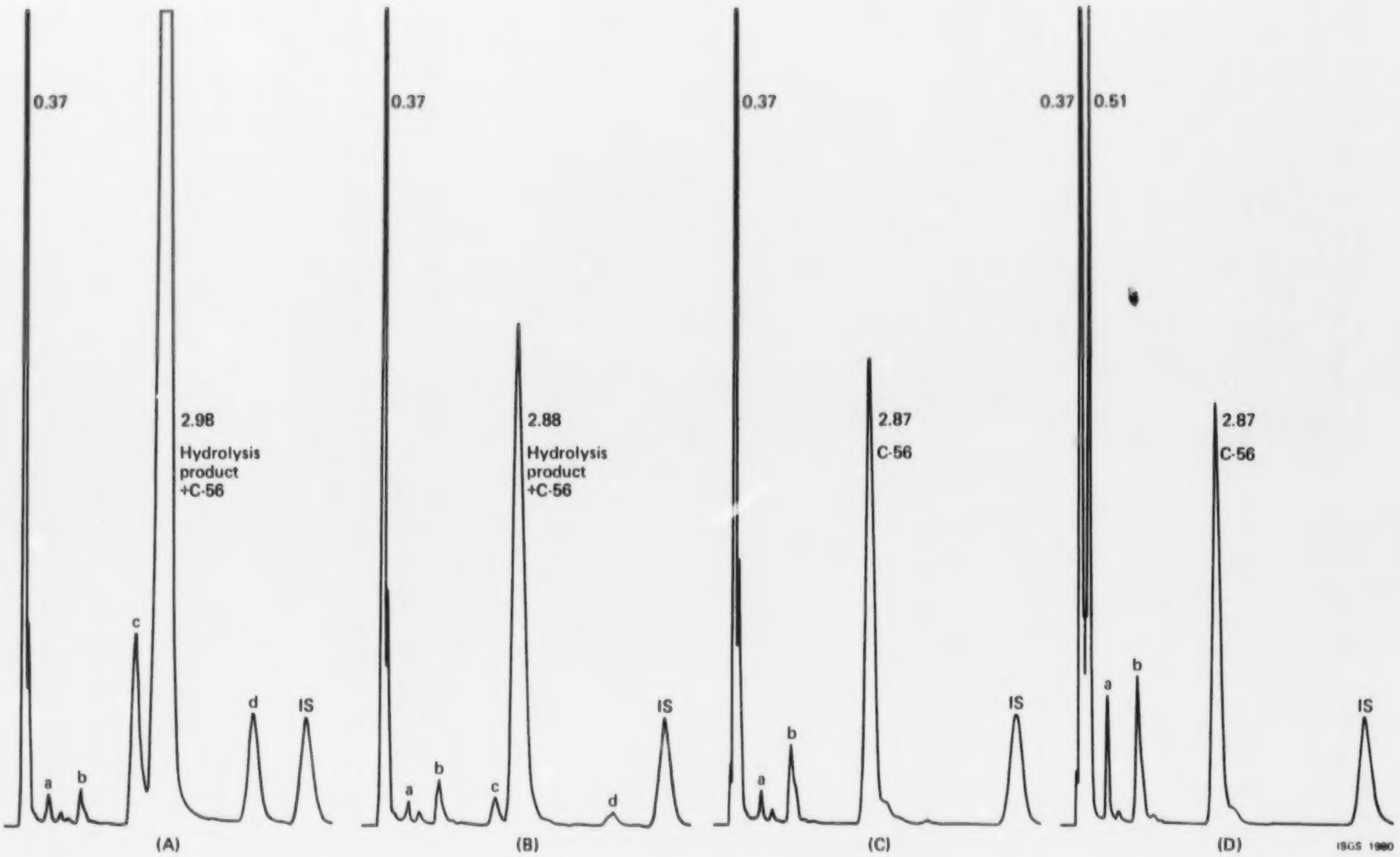
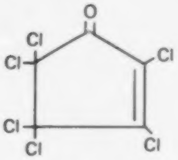


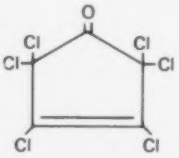
Figure 2. Packed column GC chromatograms of C-56 in tap water at various pHs adjusted with either HCl or NaOH: (A) 2.51 (B) 5.80 (C) 8.45 (original pH) (D) 11.73. IS = internal standard.

Identification of Degradation Products of C-56 in Water

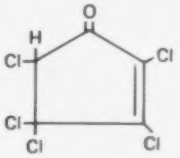
The mass spectrum obtained from the Hewlett-Packard 5985 GC/MS of the major degradation product peak in distilled water and deionized water is interpreted to contain six chlorines and to have a molecular weight of 286. The fragmentation patterns show m/e, 258 (-CO); m/e, 251 (-Cl); m/e, 223 (-CO, -Cl); m/e, 216 (2-Cl); m/e, 181 (-3Cl); m/e, 188 (-CO, -2Cl); m/e, 153 (-CO, -3Cl); m/e, 118 (-CO, -4Cl); and m/e, 111 (-5Cl). We expect that hexachloro-2-cyclopentenone (I) and hexachloro-3-cyclopentenone (II) would have fragmentation patterns similar to the unknown degradation product. Newcomer and McBee (1949) reported that hexachlorocyclopentadiene can be converted to octachlorocyclopentadiene in the presence of Cl_2 or $AlCl_3$ and further converted to compound I and compound II. They also noted that C-56 can be converted to 2, 3, 4, 4, 5-pentachloro-2-cyclopentenone (III) in sulfuric acid solution.



(I)



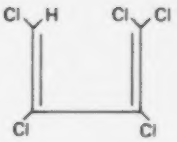
(II)



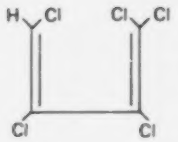
(III)

Simonov et al. (1975) also found these three hydrolysis products of C-56 in water. Compound (I) and (II) have GC retention times very close to C-56; however, separation was achieved and their presence was confirmed by using high resolution glass capillary column GC techniques (see Figure 1).

In the mineralized water (tap water) sample, the two major transformation products were different from those in the distilled water and deionized water samples. They were isomers of C_4HCl_5, and are thought to be



and



In the hydrolysis and photolysis studies, one of the degradation product peaks was found to have the same GC retention time as that of 2, 3, 4, 4, 5-pentachloro-2-cyclopentenone (III). In acidified aqueous extracts of C-56, one peak also matched a second standard, pentachloro-*cis*-2, 4-pentadienoic acid. Both compounds have previously been reported by Russian workers (Simonov et al., 1975) in a study of C-56 hydrolysis promoted by various metals. Zepp et al., (1979) suggested that tetrachlorocyclopentadienone is a major hydrolysis and photolysis product. However, we did not find this component present in our samples.

Adsorption

The results for C-56 adsorption by various soil materials used in this study are shown in Figures 3 and 4. All data were fitted by linear regression to the log form of the empirical Freundlich adsorption equation:

$$\log \frac{X}{M} = \log K_f + \frac{1}{n} \log C$$

Where X = μg of compound adsorbed; M = weight of adsorbent (g); C = equilibrium concentration of the solution (μg/mL); K_f and 1/n are constants.

Values of K_f and 1/n were obtained from the regression equations as the intercepts at a concentration of 1 ppm and the slope, respectively. These Freundlich parameters and the regression coefficient (r^2) are shown in Table 5. All the regression lines generated had coefficients (r^2) of at least 0.98, which indicate an excellent fit of the data by the Freundlich equation. The molar K, (K_F) is also shown in Table 5. It was calculated from mass K, (K_f) by using the equation described by Osgerby (1970):

$$K_F \text{ (molar)} = \frac{K_f \text{ (mass)} \times \text{Mol. Wt.}^{1/n}}{\text{Mol. Wt.}}$$

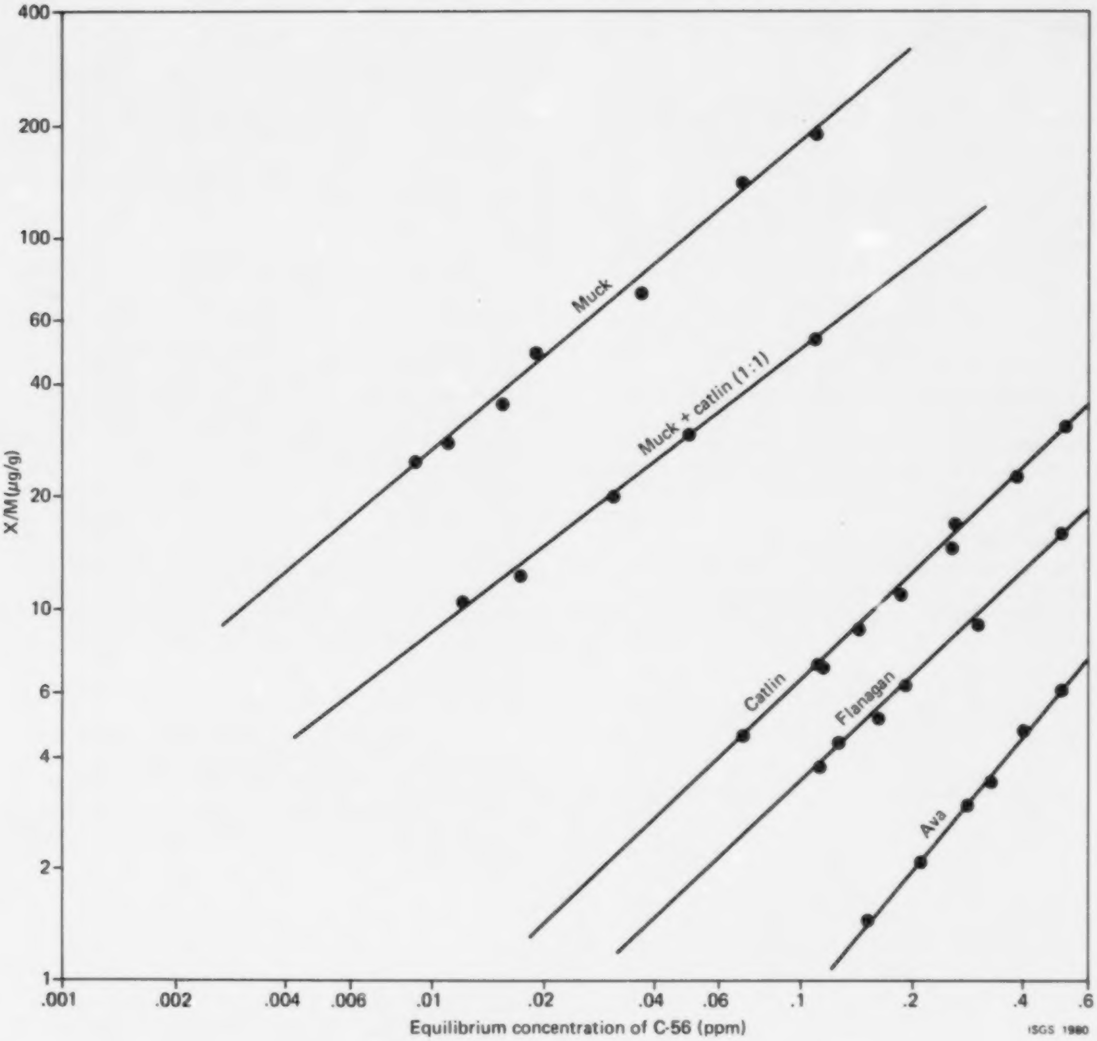


Figure 3. Freundlich adsorption isotherms of C-56 adsorption on four soil materials from tap water at 22° ± 1°C.

Where Mol. Wt. is molecular weight of the compound, K (mass) is the Freundlich K_f, and 1/n is the slope of the isotherm plotted according to the Freundlich equation. The adsorption of C-56 on these four soils followed the series:

muck > muck + Catlin (1:1)>
Catlin > Flanagan > Ava

This suggests a relationship between the organic carbon content of these soils and their adsorption capacity for C-56. The adsorption of C-56 on four clays followed the series: Ca-bentonite > illite > montmorillonite > kaolinite. This again suggests a similar relationship between the organic carbon content of these clays and their adsorption capacity for C-56.

The relationship between total organic carbon content of the nine adsorbents and adsorption of C-56 by the earth materials was investigated. The molar K (K_F) plotted as a function of TOC in percent is shown in Figure 5. A high correlation was found with a linear regression relation of

$$K_F = 8.92\ (\%TOC) + 0.78 \quad (r^2 = 0.99).$$

Similar results for PCBs, PBBs, and HCB were reported elsewhere (Lee et al., 1979; Griffin and Chou, 1980).

These results indicate that the adsorption properties of soil materials for C-56 can be predicted accurately when the TOC content of the involved earth materials are known. This information should be used with caution, however, because only a limited number of soil materials were used to develop the equation.

Mobility

The mobility of C-56 in soils expressed as R_f values is summarized in Table 6. The results showed that under the conditions tested, C-56 stayed fairly immobile in all soils when leached with tap water and landfill leachate. However, C-56 was highly mobile when leached with an acetone/water mixture, pure acetone, methanol, and dioxane. In a separate study, we also found that C-56 was immobile in Catlin, Ava, and Bloomfield soils when leached with caustic-soda brine solution.

It is interesting to note that mobility of C-56 in soil was proportional to the soil organic carbon content. C-56 was significantly more mobile in the low organic matter sandy soil than in the muck soil. Clay content does not appear to be a significant factor affecting mobility of C-56 except as it pertains to hydraulic conductivity.

In a soil column leaching study, a sample of Bloomfield loamy sand, which had been heavily spiked with C-56 to simulate a C-56 spill, was leached with 192 inches of tap water. We found 0.0005% of the C-56 was leached from this highly contaminated soil by the percolating water. However, caution should be taken because some of the hydrolysis products of C-56 described in the previous sections apparently have much higher solubility in water

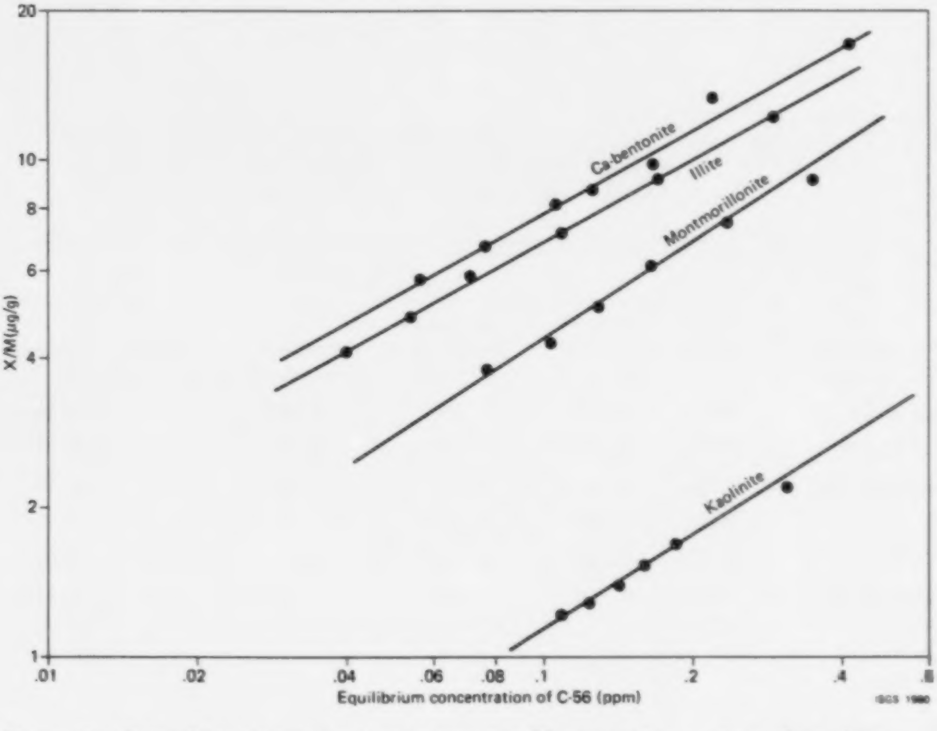


Figure 4. Freundlich adsorption isotherms of C-56 adsorption on four clays from tap water at 22° ± 1°C

TABLE 5. FREUNDLICH K_f (μg/g), 1/n, REGRESSION COEFFICIENT (r^2), AND MOLAR K_F FOR ADSORPTION OF C-56 BY VARIOUS ADSORBENTS FROM TAP WATER AQUEOUS SOLUTION AT 22°C

	Freundlich parameters			
Adsorbents	K_f	1/n	r^2	K_F
Houghton muck	1045	0.79	0.9854	322
Muck + Catlin sil (1:1)	284	0.76	0.9962	74
Catlin sil	54	0.94	0.9971	39
Flanagan sicl	28	0.92	0.9944	18
Ava sicl	13	1.18	0.9940	36
Ca-bentonite	32	0.63	0.9838	4.00
Illite	24	0.55	0.9991	1.93
Montmorillonite	18	0.60	0.9928	1.91
Kaolinite	4.4	0.58	0.9924	0.42

TABLE 6. MOBILITY OF HEXACHLOROCYCLOPENTADIENE IN SEVERAL SOIL MATERIALS LEACHED WITH VARIOUS SOLVENTS AS MEASURED BY SOIL TLC

	R_f value*					
Soil materials	Tap water	Landfill leachate	Acetone/water (1:1)	Methanol	Acetone	Dioxane
Muck soil	0.002	0.005	0.093	0.053	0.137	0.640
Catlin sil	0.002	0.002	0.793	0.879	0.972	0.989
Flanagan sicl	0.001	0.002	0.841	0.893	0.994	0.993
Ava sicl	0.002	0.003	0.871	0.891	0.990	0.956
Bloomfield ls	0.002	0.004	0.869	0.972	0.981	0.992
Ottawa sand	ND**	0.003	0.903	ND	ND	0.978

*Computed from statistical peak analysis of data by using values of 1st moment for grouped data.

**ND = Not determined.

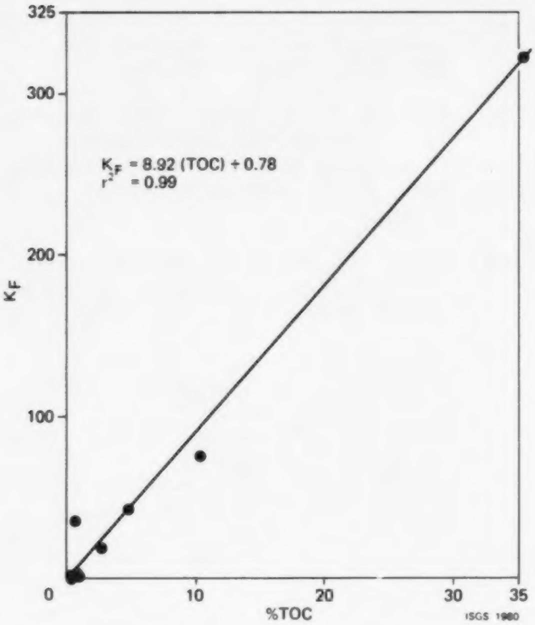


Figure 5. K_F vs TOC for C-56 adsorption by nine soil materials.

than C-56 and are much more mobile in soil. A general conclusion from this study is that C-56 mobility appears to be predictable from the TOC content of soils and that the secondary products of C-56 might tend to migrate through soils and similar natural environments and may generate problems rather than C-56 itself.

Acknowledgments

The authors wish to acknowledge partial support of this project under Grant No. R806335-010 from the U.S. Environmental Protection Agency, Cincinnati, OH; Dr. Michael Roulier, project officer.

The authors also wish to thank Dr. R. Larsen of the University of Illinois for aid in the mass-spectral analysis.

REFERENCES

1. Atallah, Y. H., D. M. Whitacre, and R. G. Butz. 1980. Fate of hexachlorocyclopentadiene in the environment. ACS preprints, 180th National Meeting, San Francisco, California.

2. Bell, M. A., R. A. Ewing, and G. A. Lutz. 1978. Review of the environmental effects of mirex and kepone. Prepared for the U.S. Environmental Protection Agency. Office of Research and development, by Battle Columbus Laboratory. EPA 600/1-78-013.

3. Griffin, R. A., F. B. DeWalle, E.S.K. Chian, J. H. Kim, and A. K. Au. 1977. Attenuation of PCBs by soil materials and char wastes *in* "Management of Gas and Leachate in Landfills." S. K. Banerji [Ed.] U.S. Environmental Protection Agency, Cincinnati, OH 45268. EPA 600/9-77-026. p. 208-217.

4. Griffin, R. A., and S.F.J. Chou. 1980. Disposal and removal of halogenated hydrocarbons in soils. Proceedings of the 6th Annual Solid and Hazardous Waste Research Symposium. U.S. Environmental Protection Agency, EPA 600/9-80-010. p. 82.

5. Hoecker, J. A., P. R. Durkin, A. Hanchett, L. N. Davis, and W. M. Meylan. 1977. Information profiles of potential occupational hazards. NTIS No. PB-276 687/OSL, 334 pp.

6. Lee, Mc., R. A. Griffin, M. L. Miller, and E.S.K. Chian. 1979. Adsorption of water-soluble polychlorinated biphenyl Aroclor 1242 and used capacitor fluid by soil materials and coal chars. J. of Environmental Science and Health A14, p. 415-442.

7. Liu, P. Y., R. L. Metcalf, A. S. Hirwe, J. W. Williams. 1975. Evaluation of environmental distribution and fate of hexachlorocyclopentadiene, chlordane, heptachlor, and heptachlor epoxide in laboratory ecosystem. J. Agr. Food Chem. 23(5):967-973.

8. Masterton, W. L., and T. P. Lee. 1972. Effect of dissolved salts on water solubility of lindane. Environmental Science & Technology, 6(10), 919-921.

9. National Academy of Sciences. 1978. Kepone/mirex/hexachlorocyclopentadiene: An environmental assessment. 78 pp.

10. Newcomer, J. S. and E. T. McBee. 1949. The chemical behavior of hexachlorocyclopentadiene. I. Transformation to octachloro-3a, 4, 7, 7a-tetrahydro-4, 7-methanoindene-1, 8-dione. JACS 71, p. 946.

11. Osgerby, J. M. 1970. Sorption and transport processes in soils. S.C.I. Monograph No. 37, Society of Chemical Industry, London, S.W. 1 p. 63-78.

12. Spehar, R. L., G. D. Veith, D. L. DeFoe, and B. V. Bergstedt. 1979. Toxicity and bioaccumulation of hexachlorocyclopentadiene, hexachloronorbornadiene and heptachloronorbornene in larval and early juvenile fathead minnows, *Pimephales promelas*. Bull. Environ. Contam. Toxicol. 21, p. 576-583.

13. Setchenow, M., 1892. Action De L'Acide Carbonique Sur Les Solutions Des Sels. Ann. Chem. Phys. V. 25:226.

14. Simonov, V. D., et al. 1975. Hydrolysis of hexachlorocyclopentadiene. Vsesoiuznoe Khimicheskoe Obshehestvo Imeni D. I. Mendeleeva Zhurnal, v. 20, p. 477.

15. Yu, C. C., and Y. H. Atallah. 1977. Velsicol Chemical Corporation Project 482428 report Nos. 1, 2, and 3.

16. Zepp, R. G., N. L. Wolfe, and G. L. Baughman, P. F. Schlotzhaner, and J. N. MacAllister. 1979. Dynamics of processes influencing the behavior of hexachlorocyclopentadiene in the aquatic environment, American Chemical Society Preprints, 178th National Meeting, Washington, D. C. Sept. 9-14.

METHODS OF SOIL HYDRAULIC CONDUCTIVITY DETERMINATION AND INTERPRETATION

David W. Roberts and Michael A. Nichols

ABCDirt
Soil Scientists
Seattle, WA 98103

ABSTRACT

Section 3004 of the Resource Conservation and Recovery Act mandates the promulgation of standards for the location, design and construction of hazardous waste treatment, disposal or storage facilities. Such legislation deals with the land disposal of industrial or hazardous wastes and focuses on the potential water pollution that can result from such practices because more than half the U.S. relies on ground water for their drinking supply. This paper provides a look at the categories of water movement that occur in connection with various types of land-based disposal systems, some background information and general equations relating to soil water movement, a brief summary of soil testing methods divided into saturated and unsaturated sections with subsections of laboratory and field techniques, a soil testing methods matrix that attempts to evaluate the applicability of individual tests for solving various soil water movement problems, and some remarks regarding the present status of available information, what is trying to be obtained in the future, and how do we get there from here.

INTRODUCTION

As more and more waste is being applied to land, the question of where it goes and how fast it gets there needs to be answered better than has been done in the past, as it is apparent that some sites have not been well-designed in accordance with soil hydrological properties.

Considering the array of waste materials and the different modes of application, there appears to be three categories of water movement that come into play. First of all is the consideration of water movement within the root zone when crops are grown as part of the treatment-disposal system. Such waste streams as municipal and industrial wastewaters, sludges, and some hazardous wastes are materials that may be applied to the soil surface or injected into the rootzone. One big advantage of such systems is in the way that plants can use or immobilize both water and contaminants/nutrients.

A second type of water movement relates to use of compacted soil layers as liners for landfills and surface impoundments. Since such soil is disturbed by mechanical equipment it will no longer behave the same hydraulically as it did in its undisturbed state.

A third type of water movement related to waste disposal sites is the unsaturated zone between the root zone (or liner) and the ground water table or bedrock as water movement will be very different in subsoil materials than in surface horizons.

In this paper we intend to discuss some of the basic principles involved in water movement in soil with a brief look at several types of soil testing methods for both laboratory and field varieties of saturated and unsaturated hydraulic conductivity determination. After this discussion the available information on advantages, disadvantages, and limitations has been compiled into a soil testing methods matrix that attempts to rate the applicability of each individual test for the three types of water movement, problems that may arise in considerations of waste applications to land. The final part of this paper is a look at what can be expected in the future.

WATER MOVEMENT

Water movement in soils can be divided into two types of flow systems for general consideration: (1) saturated flow where all pores are filled with water and (2) unsaturated flow where both air and water are present in the pores.

The basic equation for describing water flow through porous materials, whether saturated or unsaturated flow, is expressed by Darcy's Law:

$$J = K \cdot \Delta H$$

where: J = flux or volume of liquid moving thru a cross-sectional area of soil per unit of time

K = hydraulic conductivity, and

ΔH = hydraulic gradient = $\frac{dH}{dx}$ where dH = difference in hydraulic potential and dx = difference in distance over which the difference in hydraulic potential is measured.

The hydraulic conductivity, K, is not constant for a given soil as it can vary with changes in the water content as well as changes in the pressure head. Therefore, the hydraulic conductivity can either be expressed as a function of water content, $K(\theta)$ or as a function of pressure head, $K(h)$. For determination of either function, the soil moisture characteristic/retentivity curve/water capacity function ($\theta(h)$) usually must be known also. Figure 1 demonstrates these two different cases: A) Soil moisture characteristics for four soils with the respective hydraulic conductivity curves expressed as a function of pressure head and B) Soil moisture characteristics for one soil and its hydraulic conductivity relation expressed as a function of water content.

Saturated Flow

The determination of saturated hydraulic conductivity is physically easier and conceptually simpler than the determination of unsaturated hydraulic conductivity because the purpose is to find the hydraulic conductivity at only one point, ($h = 0$, θ = constant), rather than over the range of pressure heads or range of water contents necessary for unsaturated flow determination. Therefore, at saturation it is assumed that all the soil pores are constantly and completely filled with water and that the hydraulic conductivity is a constant. This is shown graphically in the right part of Fig. 1(A) where the saturated conductivity for each soil is where their respective curves intercept the y-axis.

However, in a given soil, the saturated hydraulic conductivity may not remain constant over time due to processes such as particle rearrangement within the soil matrix. Also, depending on the mode of wetting, saturated soils rarely have all soil pores completely filled with water. It is not unusual to expect 2-12% air remaining in the soil pores (Yong & Warkentin, 1975). This implies that attention should be placed on the mode of saturation because if K is determined for a situation of entrapped air, it is basically an unsaturated flow situation, and unsaturated flow will always be less than saturated flow.

Unsaturated Flow

The situation for unsaturated hydraulic conductivity determination is more complex than for saturated flow because the purpose is to determine a complete hydraulic conductivity function over a range of pressure heads or water contents rather than the one-point analysis as for saturated flow.

Another concept that should be introduced to the discussion of unsaturated flow is diffusivity which can be expressed as:

$$D(\theta) = K(\theta)\,\frac{dh}{d\theta} = \frac{K(\theta)}{C(\theta)}$$

where $D(\theta)$ = soil water diffusivity as a function of water content

$K(\theta)$ = hydraulic conductivity as a function of water content

$C(\theta)$ = water capacity/retentivity/soil moisture characteristics as a function of water content

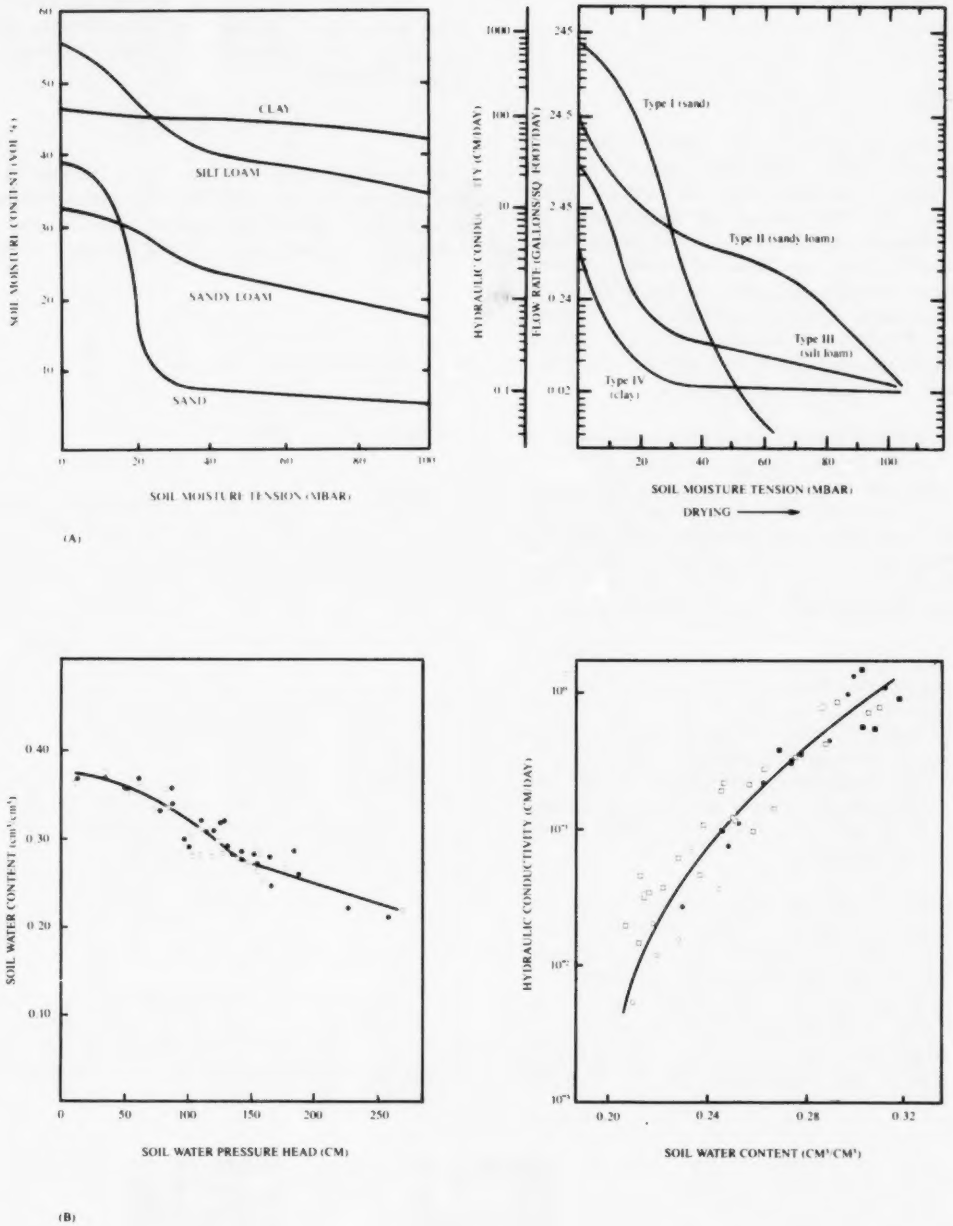


Figure 1. Water retention curves and hydraulic conductivity. (A) Water retention curves and hydraulic conductivity as a function of pressure head (SSWMP, 1978) and (B) water retention curve and hydraulic conductivity as a function of water content (Flocker et al., 1968).

$\frac{dh}{d\theta}$ = reciprocal of slope of $C(\theta)$ function at a particular water content.

Anisotrophy

Anisotrophy is the term used to describe the fact that soil properties can vary with depth as well as in horizontal direction. Such differences are the result of weathering of rocks or sedimentary bodies and the reorganization, translocation, and concentration of the more mobile constituents due to the effects of the environment (Brewer, 1976). Unfortunately, anisotrophy in soils is the rule rather than the exception, which will affect soil testing methods and their interpretation.

Soils are stratified formations consisting of distinct layers (horizons) which have differences in particle size distributions, structure, boundary conditions, and other properties which affect the hydraulic properties of each horizon and macroscopic level (soil series) as well as on the microscopic level (soil fabric). Such differences will influence water movement in soils.

At the soil series level, anisotrophy is manifested in two ways: (1) horizons will vary in depth as well as thickness and can exhibit anomalies such as vertical sand seams or clay lenses and (2) boundary conditions between soil horizons can sometimes influence overall hydraulic conductivity more than the properties of the mass of the horizon itself. This is shown graphically in Figure 2.

In Case A, water added to the sand will flow through the sand quickly into the clay, while in Case B, no water will enter the sand layer until the clay layer is nearly saturated because the water is held by the finer pores in the clay horizon. Therefore, the clay horizon in Case B might hold up to two or three times as much water as the upper clay horizon in Case C.

Further, anisotrophic conditions can affect the direction of water movement as there are both horizontal and vertical components to the hydraulic conductivity function. Given the Darcy equation:

$$J = K \cdot \angle H = K\frac{dH}{dx}$$

and knowing that the hydraulic potential H = the sum of the gravitational (2) and pressure (h) potentials, expressions can be derived for both the horizontal and vertical components of flow.

for horizontal flow: $J = K \cdot \frac{dh}{dx}$

where J = flux

K = hydraulic conductivity

$\frac{d(2+h)}{d_3}$ = change in pressure potential divided by change in distance

for the vertical flow: $J = K \cdot \frac{d(2+h)}{d_3}$

where J = flux

K = hydraulic conductivity

$\frac{d(2+h)}{d_3}$ = change in sum of gravitational and pressure potentials divided by change in gravitational potential

A review of the literature for the ratio of horizontal K to vertical K for fine-textured soils reveals ratios of 0.7 to 40 with a common range of approximately 1 to 4 (Roberts and Nichols, 1980).

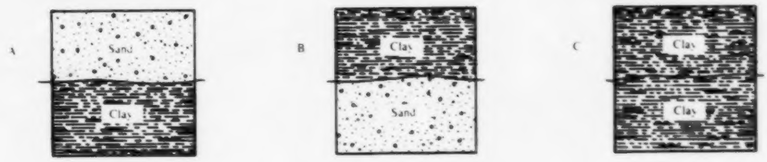


Figure 2. Influence of underlying layer on hydraulic conductivity.

At the microscopic level, soil fabric will also exhibit anisotrophy which can cause substantial hydraulic conductivity anisotrophy. Mitchell (1976) states. "Of the properties of importance in the analysis of geotechnical problems of fine-grained soils, none is more influenced by fabric than the hydraulic conductivity." Also, initial fabric anisotrophy may cause mechanical property anisotrophy with spatial and vertical differences being significant.

Further, fabric anisotrophy may be developed in initially homogeneous soils from shear or compression forces. The amount of shear or compression required for development of anisotrophic fabric varies for mineral soils, and depends on such factors as soil mineralogy, composition of pore fluid, and initial fabric (Mitchell, 1976).

A practical ramification of soil fabric anisotrophy is that the hydraulic conductivity of a dry soil is dependent on the structure and fabric to such an extent that analyses based on properties determined from the same material but with a different structure may be totally in error. That is, where fabric and isotrophy can affect a parameter being tested (such as the hydraulic conductivity of clay soils), laboratory results often may not reproduce field results due to sampling and preparation procedures of laboratory methods which will change soil fabric. Therefore, extrapolation of laboratory results to field conditions should only be used with caution and supporting justifications.

Hysteresis

Another phenomenon that should be mentioned under the topic of water movement is hysteresis which is a term describing the fact that the water capacity/retentivity/soil moisture characteristic is different for when the soil is drying than when the soil is being wetted. Said another way, it is harder to get water out of the soil once it is in, than to get it back in once it is out. Figure 3 depicts this phenomenon and shows that the water content of a soil at a given suction will be greater following desorption (drying) than following adsorption (wetting).

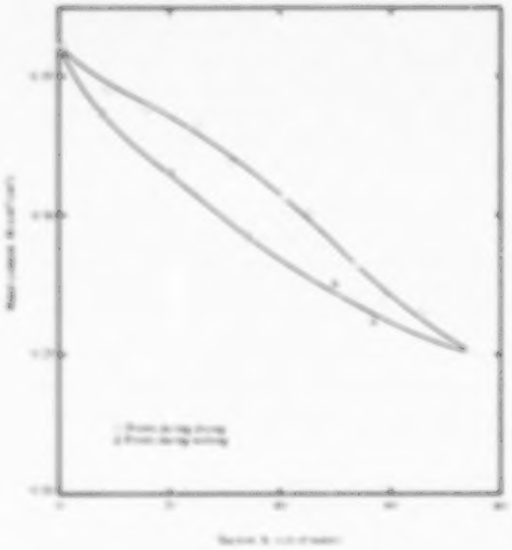


Figure 3. The relations between water content (θ) and suction (h) (Tzimas, 1979)

Since the moisture retention curves are usually determined by a desorption process starting with a saturated soil, values thus obtained may not apply to water contents and moisture potentials occurring in the field when an initially dry soil is wetting up. However, a physically correct characterization of the extent of hysteresis on a given soil is a very elaborate procedure (Gillham et al., 1976).

SOIL TESTING METHODS

Like the breakdown of water movement into saturated and unsaturated flow, the soil testing methods are also divided into these same sections with further distinctions between laboratory and field methods.

Saturated Flow -- Laboratory Methods

The pressure cell technique is a method where an undisturbed core, or disturbed volume of soil, is placed in a metal pressure cell. After the soil is initially saturated, it is connected to a standpipe where a falling head procedure allows water to move through the pressure cell (Klute, 1965a).

The compaction mold technique is a method where disturbed soil is compacted in a standard compaction mold and then placed in a pan of water and allowed to saturate. A falling head technique can be utilized or pressure can be used to speed up testing time. The volume of water is recorded over time (Matrecon, 1980).

There are two ways to use consolidation cells to determine hydraulic conductivity. One method employs direct measurement by means of a falling head permeameter of special design used in connection with the consolidation test. A second method relies on the use of the coefficient of compressibility, the coefficient of consolidation, and the void ratio in consolidation theory to calculate hydraulic conductivity (Means andParcher, 1963).

The triaxial apparatus technique is very similar to the consolidation cell method as the hydraulic conductivity can be determined directly from water flow measurements in the triaxial apparatus, or the hydraulic conductivity can be calculated from consolidation theory (Matyas, 1967).

The micromorphometric data technique is a calculation method which is very different from the other procedures for determination of saturated hydraulic conductivity. Rather than using any measurement of flow or flux, characterization of planer slits and tubular pores at a microscopic level by freeze-drying techniques for thin sections and scanning by a Qantimet computer are used to predict saturated hydraulic conductivity (Bouma et al., 1979).

Saturated Flow -- Field Methods

The piezometer method is based on the measurement of flow into an unlined cavity at the lower end of a lined hole. Water entering the unlined cavity and rising in the lined hole is removed several times by pumping or bailing to flush the soil pores along the cavity wall. After flushing is completed, the water is allowed to come to equilibrium with the water table (Boersma, 1965a).

It should be noted here that there are several varieties of 'piezometer' tests used, depending on the geometry and materials located at the point of measurement. Besides the cylindrical cavity outlined in this procedure, there are spherical cavities, sand-filled cavities, piezometer tips placed in sand-filled cavities, or piezometer tips pushed directly into the soil. This last method (Jezequel and Miuessens, 1975) looks especially promising for evaluation of the low conductivities of clay soils.

The double ring infiltrometer technique is a method where two open metal cylinders, one inside the other, are driven into the soil (from a few centimeters to several feet) and partially filled with water that is maintained at a constant level in both rings. The amount of water added to maintain the constant water level is the measure of the volume of water that infiltrates the soil. This volume can be measured over time and thus be expressed in cm hour^{-1} (Bertrand, 1965; ASTM D 3385-75).

A modification of the double ring infiltrometer called the permeameter method uses the sides of a hole to make the outer ring with a smaller metal cylinder positioned in the center. There is a constant water supply system that maintains the water level in the cylinder and in the surrounding hole. This method also employs the use of tensiometers to indicate saturated conditions (Boersma, 1965b).

Cased boreholes are performed by pumping water into a borehole (infiltration test) or out of a borehole (drawdown test) with or without the use of inserts. These tests may be conducted as a constant head test in which the rate of pumping which is necessary to maintain a constant water level in the borehole is measured. Alternatively, a variable head test may be performed by observing the change in water level in the borehole after inflow has stopped. Fully or partially cased boreholes are usually employed in these methods. The hydraulic conductivity of a localized zone of soil surrounding the base and uncased portions of the borehole is computed by the application of theoretically derived equations.

Well pumping tests are performed by pumping water into or out of a screened well embedded below the natural ground water table. As pumping progresses, the resulting change of ground water level is monitored in surrounding observation wells. Generally, four or more such observation wells are employed. Pumping tests may be categorized as equilibrium (steady state) or non-equilibrium (transient flow) tests (Milligan, 1975).

In an equilibrium pumping test, the ground water level measurements are recorded once a constant water level has been attained in the observation wells. In the non-equilibrium test, the rate of pumping and the consequent rate of water level change in the observation wells are recorded. The advantages of transient flow testings are that testing time may be reduced as compared with equilibrium testing, and ground water drawdown may be controlled or halted if necessary.

Unsaturated Flow -- Laboratory Methods

Steady state techniques are methods where the hydraulic conductivity is measured by applying a constant hydraulic head difference across the sample contained in a soil core and measuring the resulting steady state flux of water. The flow rate, Q, and tensiometric metric potentials (pressure head) are recorded.

There are two varieties of steady state tests often referred to as the short or long column method. The short column method utilizes columns of 10-15 cm while the long column variety uses lengths of 50-200 cm. An advantage of the long column technique over the short column is that more than two tensiometers are encased along the side of the longer column which will allow the determination of the head difference across each interval and thus the hydraulic conductivity function for each section or layer (Klute, 1965b; 1972).

In the pressure outflow method (Klute, 1965c) the time dependence of the outflow of water from a soil core on a porous plate or membrane in a pressure cell is used to determine the soil-water diffusivity (D).

Hydraulic equilibrium is first established in a layer of soil (usually 1-5 cm in depth), with the gas phase pressure in the cell at a given level. Beginning at or near saturation, step increases of gas pressure are applied to produce an outflow of water, and the volume of outflow as a function of time is measured. Paired values of diffusivity and water content are obtained from each pressure increment and thus the drainage function, $D(\theta)$, can be plotted. Since the total volume of outflow and the pressure head increment corresponding to each gas phase pressure increment are known, the water capacity can be obtained and used to calculate hydraulic conductivity from the relationship: $K = DC$ where K = hydraulic conductivity (cm sec^{-1}), D = diffusivity (cm^2 sec^{-1}), and C = water capacity (cm^{-1}).

The movement through impeding layer technique is a vertical infiltration method that makes use of the hydraulic resistance of a membrane or crust at the soil surface to produce negative pressure-head values in the soil just below the impeding layer. The lower the hydraulic conductivity of the crust, the more negative the pressure head in the soil. To obtain a weighted mean diffusivity, D, and hydraulic conductivity, K, as a function of water content, θ, a series of columns, each capped by a crust or porous plate of different hydraulic resistance is required. A constant shallow head of water is then applied to the top of the impeding layer, and the rate of infiltration is measured (Hillel and Gardner, 1970).

The instantaneous profile technique is a method that can be used in the laboratory or in the field. In the laboratory, a flow system (usually a soil column) is established whereby the inflow or outflow, water content, and pressure head are measured or inferred (Watson, 1966).

Basically, there are three options with respect to measurements made on the flow system: (1) the water content and pressure head distributions may both be measured, (2) the water content distribution may be measured and the pressure head inferred from water retention data, or (3) the pressure head distribution may be measured and the water content inferred from water retention data.

Unsaturated Flow -- Field Tests

The crust technique is a field adaptation of the laboratory procedure for flow through an impeding layer. The crust test can be used to determine both saturated and unsaturated conductivity (SSWMP, 1978).

The crust test method requires carving out a cylindrical pedestal of soil, whose upper surface is at the depth where the hydraulic conductivity is desired. A ring infiltrometer of the same diameter as the pedestal is firmly affixed to the top of the pedestal so that the soil's horizontal surface is enclosed by the ring. A paste consisting of gypsum and sand, mixed with a small amount of water, is spread over the entire horizontal surface and is allowed to harden, forming a crust. When water is introduced through the infiltrometer and maintained at a constant head, flow into the soil is restricted by the crust. A constant, steady state flow rate is established, inducing a nearly uniform moisture potential (measured by tensiometers) and the steady state flow rate (measured at the infiltrometer with a burette) defines a plot of infiltration vs. soil moisture tension (the K(h) curve). Crusts of different resistances yield different points on the K(h) curve. A series of crusts ranging from greater to lower resistance assures that the data points fall on the wetting curve.

The technique can be extended to include measurement of saturated hydraulic conductivity which requires the addition of a barrier to flow around the sides of the soil pedestal. This is usually done with the soil pedestal thoroughly wetted and with a slurry of dental grade plaster applied to the sides. No crust is applied to the surface in this case.

The traditional instantaneous profile technique in situ is a method where a nearly level plot of soil is diked to pond 2-3 cm of water. After addition of water the plot is covered to prevent evaporation, and drainage occurs. At frequent intervals both pressure head and water content values are measured. From these measurements, instantaneous values of the pressure gradients and fluxes can be determined, which will also provide hydraulic conductivity values (SSWMP, 1978).

The unit gradient-drainage method is a type of instantaneous profile method where the soil is wetted deeply and allowed to drain while evaporation is prevented. In a uniformly draining soil profile, the hydraulic gradient is often nearly unity, and the water content is a function of time and nearly independent of depth. This relation can be expressed as:

$$D = L\frac{dh}{dt}$$

where D = diffusivity ($cm^2\ sec^{-1}$)
L = length (cm)
h = average hydraulic head (cm)

This method differs from the traditional instantaneous profile method in that instead of measuring both water content and pressure head in the field, only pressure head is measured in the field, and water content from laboratory-determined water retention curves is used to calculate hydraulic conductivity from the equation $K = D d\theta/dt$. Description of the unit gradient-drainage method has been reported by: Black et al., 1969; Davidson et al., 1969; Gardner, 1970; Klute, 1972; Nielsen et al., 1973; and Simmons et al., 1979.

A third method called the Libardi technique (Libardi et al., 1980) is a very recent attempt to simplify the field determination of hydraulic conductivity by means of a modified instantaneous profile method. Similar to the unit-gradient drainage method, it measures only one parameter rather than both water content and pressure head. However, unlike the unit-gradient drainage method, the other parameter is not measured in the laboratory. In fact, in the Libardi method only the neutron probe device is used for water content measurement, and hydraulic conductivity is determined without any further information.

Because of various difficulties involved in the direct measurement of the hydraulic conductivity function, there has been considerable interest in the potential of calculating the conductivity from the other properties of the medium that may be easier to measure such as the pore size distribution or the water retention curve. The basic concepts are given by Childs and Collis-George (1950), Marshall (1958), and Milligan-Quirk (1960, 1961, 1964). Since there is quite a variety in the approaches taken and lack of space here for elaboration, the reader is referred to Roberts and Nichols (1980) for brief summaries of a number of such research efforts.

ADVANTAGES, DISADVANTAGES AND LIMITATIONS OF TESTS

Laboratory Tests

The main advantages of laboratory testing are economy and convenience. Laboratory tests offer financial benefits accruing from the fact that a large number of tests can be performed routinely in a well-equipped soil testing laboratory. Also, such testing can be performed by technicians, in contrast to the generally higher level of skill required for the execution and interpretation of field testings. Laboratory testing offers protection from adverse weather conditions. They can be performed at all times, while field testing is necessarily restricted to non-rainy, unfrozen seasons, which generally means it must be performed during the summer. However, such advantages are offset by an array of disadvantages.

Limitations of Laboratory Tests

Olson and Daniel (1979) have listed potential sources of error in laboratory tests for both saturated and unsaturated flow. These lists are presented in Table 1.

TABLE 1. SOURCES OF ERROR IN LABORATORY TESTING FOR SATURATED AND UNSATURATED FLOW (Olson and Daniel, 1979)

Saturated	Unsaturated
(1) Non-representative samples	(1) Non-representative samples
(2) Voids formed during sample preparation	(2) Smear zones
(3) Smear zones	(3) Incorrect flow direction
(4) Alterations in clay chemistry	(4) Growth of microorganisms
(5) Air in sample	(5) Chemical effects
(6) Growth of microorganisms	(6) Temperature effects
(7) Meniscii problems in capillary tubes	(7) Filter impedance
(8) Use of excessive hydraulic gradients	
(9) Temperature effects	
(10) Volume change due to stress change	
(11) Flow direction	

Of these possible sources of error, of greatest concern is the use of samples that may not be representative of field conditions. Disturbed samples that are taken back to the laboratory and repacked in the various types of apparati will not have the same fabric, structure, or pore configuration as they did in their undisturbed state. Additionally, the use of small samples compounds the disturbed soils problem by omitting macroscopic variations occurring at the field level such as sand lenses, fissures and joints, and root holes. Therefore, since laboratory tests are deficient with regard to both microscopic and macroscopic features of the soil in the field, extreme caution is urged with regard to laboratory results' extrapolation to the field scale level.

Comparison of Laboratory to Field Testing Results

A comparison of corresponding laboratory and field hydraulic conductivity test results will show the field hydraulic conductivity to be considerable, but unpredictably higher than values measured in the laboratory. Olson and Daniel (1979) compared field and laboratory hydraulic conductivity values from the literature and found that the range of the ratios of field K/laboratory K have been reported from 0.3 to 46,000 with 90% of the observations in the range from 0.38 to 64 with field results usually being higher than laboratory results. They report the major causes of this effect as being: (1) a tendency to run laboratory samples on more clayey samples, (2) the presence of sand seams, fissures, and other macrostructural features in the field that are not represented properly in laboratory tests, (3) the use of laboratory K values backcalculated from consolidation theory rather than directly measured values, (4) the measurement of vertical flow K in the laboratory and of horizontal K in the field, (5) the use of distilled water in the laboratory, and (6) air entrapment in laboratory samples.

Field Tests

While field tests have some sources of error similar to problems encountered in laboratory testing, field testing has some unique problems. One such difficulty arises from the fact that most experience in in situ soil testing has been on coarse-textured soils. Also, most of the field-scale experience of soil engineers, geohydrologists, and soil scientists has been experimental rather than standardized and has addressed problems such as ground water flow and soil - water - plant relations, and this information is not always completely applicable to the problems of hazardous waste landfills and surface impoundments.

Another problem associated with field-scale testing lies in the use of Darcy's Law in the flow analysis, in the excessive attention directed at the analysis rather than the value of K. This is an unfortunate occurrence since no other soil parameter is as likely to exhibit the wide range of values (from 10^{-1} to 10^{-10} cm sec^{-1}) as does hydraulic conductivity. Important considerations for quantification of field level hydraulic conductivity are fabric and spatial variability, as elaborated below.

Fabric

Of the parameters of significance in the analysis of environmental problems of fine-textured soils none is more influenced by fabric than hydraulic conductivity (Mitchell, 1976). A simple example of this phenomenon is provided in a consideration of two equal volumes of soil (A and B) with exactly the same properties with the exception of one long continuous pore in soil volume A and four discontinuous pores with total equivalent pore volume equal to soil volume A in soil volume B. Hydraulic conductivity will be dramatically different between these two cases.

Therefore, it is of importance that the soil testing required for site evaluation actually test the soil fabric that will exist in the landfill or surface impoundment. The tested soil fabric will be of two separate types: soil fabric of the liner and soil fabric of the unsaturated zone between the liner and ground water table or bedrock.

Soil Fabric and Soil Liners —

The importance of soil fabric to considerations of the hydraulic conductivity of soil liners cannot be overstated. In a chapter of Fabric, Structure, and Property Relationships, Mitchell (1976) states that the main conclusion to be drawn from the considerations of his chapter is that the geotechnical properties of any given soil are dependent on the structure to such an extent that analyses based on properties determined from the same material but with a different structure may be totally in error. Therefore, considerations of use of a particular soil for a liner must be based on soil testing methods that simulate the field compactive effort to the highest degree possible.

Soil Fabric in the Unsaturated Zone —

As mentioned in "Limitations of Laboratory Tests" one considerable failing of laboratory tests is that the soil fabric of the tested sample will not be the same as the fabric of the soil in situ. Lambe and Whitman (1979) state that because permeability depends very much on soil fabric (both microstructural--the arrangement of individual particles, and macrostructural---such as stratification) and because of the difficulty of getting representative soil samples, field determinations of hydraulic conductivity are often required to get a good indication of the average hydraulic conductivity.

Spatial Variation (Anisotrophy)

The soil is not a static body, but rather a dynamic set of processes always being affected by the soil-forming factors of climate, parent material, topography, vegetation, and time. Therefore, a soil body will vary in both the vertical and horizontal directions. For example, vertical variation is manifested in different hydraulic conductivities between successive soil horizons, and horizontal variation is manifested in differing thicknesses of soil horizons between soil profiles of the same soil series. Thus non-homogeneity (anisotrophy) in soils is the rule rather than the exception, and soil testing of homogenous or mixed samples for average conditions may be totally in error in predicting conditions that will exist in the field.

Additionally, during the site evaluation and review process, attention must be devoted to a qualification of errors involved in soil testing results. That is, some determination of whether the variation in soil testing results is a consequence of the soil's spatial variability or a variation inherent in the soil testing method itself. At this time, excepting the information included in Roberts and Nichols (1980) little information is available to quantify the components of variation in the results of many soil testing methods.

SOIL TESTING MATRIX

The rating of the various soil testing methods presented must be predicated upon the objectives of the results' interpretation or extrapolation. As mentioned earlier in this paper, there are three situations where water movement is important: 1) in the root zone if plants are part of the receiver system, 2) around the liner where natural soil is compacted, and 3) the unsaturated zone between root zone or liner and ground water level or bedrock. Therefore, soil testing methods should be chosen with regard to which of the three types of water movement will be most important in a proposed waste disposal site.

Table 2 is an attempt to rate the applicability of the various soil testing methods for 1) root zone movement with crops, 2) liner evaluation, and 3) the unsaturated zone between waste and ground water.

TABLE 2. SUMMARY OF TESTING METHODS

TYPE OF TEST	Root Zone	Liner	Unsat. Zone	Comments
SATURATED-LABORATORY				
pressure cell	3	3	4	small sample; only saturated K
compaction mold	3	1	4	simulates remolded soil liner and waste; only saturated K
consolidation cells	3	2	4	simulates remolded soil liner; only saturated K
triaxial apparatus	3	2	4	simulates remolded soil liner; only saturated K
micromorphometric data	2	2	2	only experimental at this time; potential value due to fabric quantification
SATURATED - FIELD				
piezometer	3	4	3	generally of limited value; self-boring piezometer has potential for clay soils
double ring infiltrometer	2	3	3	easy to perform; only saturated K
permeameter	2	3	3	easy to perform; only saturated K
cased boreholes	4	4	3	easy to perform; calculation of K though questionable on silts, not applicable to clays
well pumping tests	4	4	3	expensive and requires presence of ground water table; again questionable for silts and not applicable to clays
UNSATURATED-LABORATORY				
steady state (long column)	2	2	2	larger sample than short column; longer time period required; can get K for layers
pressure outflow	3	3	3	small sample; difficulties associated with age of excessive pressure heads
impeding layer	2	2	2	potential exists for use of liner material rather than crust
instantaneous profile	2	2	2	small sample
UNSATURATED-FIELD				
crust	1	3	1	both unsaturated and saturated K; potential to simulate liner in situ
traditional instantaneous profile	1	3	1	measures water content and pressure head so that $K(\theta)$ or $K(h)$ can be determined
unit gradient-drainage instantaneous profile	2	3	2	simplified instantaneous profile method; less field time than traditional method
Libardi instantaneous profile	2	3	2	less field time than unit gradient-drainage method; needs field verification

THE ABC EQUATION

Beyond the applicability of the individual testing methods for the three types of water movement of concern in land-based waste disposal systems, some remarks can be made regarding the present status of available information, what is the end point we are trying to obtain, and how do we get there from here.

The end product of research on soil testing methods for hydraulic conductivity determination could be a formula in the form of "a" number of "b" type of soil tests per "c" unit of land area (abc equation) that could be used on a uniform basis nationally for any proposed waste disposal sites.

However, before discussing the abc equation, one other point regarding site assessment and soil testing methods needs to be emphasized. Site assessment and soil testing methods need to interact and be performed in conjunction with each other rather than be separate and distinct segments of the longer study since test result numbers are only as good as how well the whole site is characterized. For problems of practical interest, it is clear that permeability tests (laboratory or field) must be performed with a great degree of care and attention to detail. However, just performing the tests properly still does not insure successful results. Thorough field investigation to identify zones of maximum and minimum permeability, and careful selection of samples or layers for testing, are in some respects more important than experimental technique. Even with a comprehensive field investigation and suitable experimental technique, some degree of judgment must inevitably be exercised before results are used for field predictions (Olson and Daniel, 1979). The following example can be used to illustrate this point.

The usual approach that does not integrate the site assessment into the soil testing program will take a site and place a grid over the study are as shown below with a 180-acre site having 1 test per 5 acres or 36 soil-testing locations.

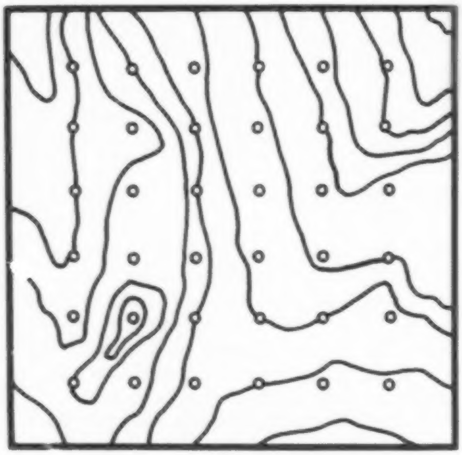


Figure 4. Site topo with testing grid.

One simple twist of the site assessment by use of Soil Conservation Service Soil Surveys which can give preliminary soils information which may eliminate some of the areas from the testing program. Show below is the soil survey of the area shown above. From preliminary study of the Soil Survey we discover that only the soil series "a" and "b" appear applicable for waste disposal. Gridding this area using the same parameters as above, we now need only 20 tests.

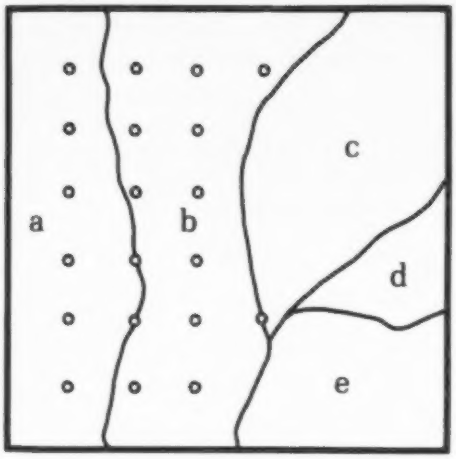


Figure 5. SCS Survey with testing grid.

However, SCS maps may lack site-specific precision due to mapping scale, usually 1:20-24,000. Thus most county soil surveys can only represent general soil bodies and not the specific soil physical and hydrological properties needed to evaluate and design land-based waste disposal systems. Since a "good" soil survey is usually considered to be 70-80% accurate with soil boundary lines within 200-300 feet, such accuracy can be further improved by the additional use of color aerial photographs and/or on-ground, detailed soil mapping or ground-truthing as shown in Figure 6. This figure shows the ABCDirt survey that utilized aerial photographs coupled with detailed soil mapping. This can be compared to the SCS map in Figure 5.

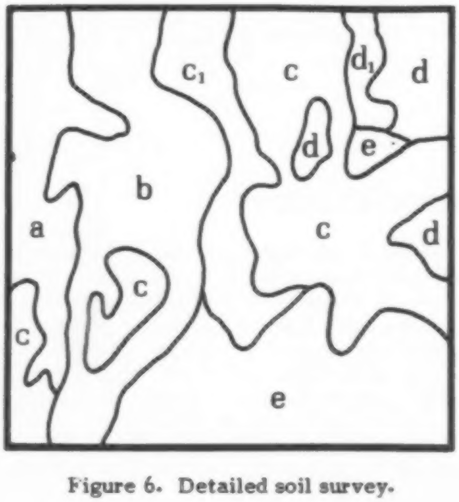


Figure 6. Detailed soil survey.

At this point it should be noted that the detailed soil survey discovered a soil series variant, "c1" which was not noted at all on the SCS Soil Survey. Since this soil was preliminarily appropriate for waste disposal, this area was included in the area to be tested.

Going one step further beyond the detailed soil survey could be the consideration of variation within each individual soil series which can help determine how many tests should be performed and where these tests should be located (such a procedure will also be useful to the monitoring system design). In this example (Figure 7) soil series "c1" proved to be very uniform and thus three testing sites were equally spread over the area. However, in soil series "b" the percent clay content in the argillic horizon was found to significantly vary in the northwesterly direction. Therefore, testing sites were located at the two extremes and one in the middle of this soil variation transect meant to represent the average or modal location for this soil property, clay percentage. Extended out from the modal site are soil property isotherms intended to represent similar properties to the modal site which will help to statistically support the soil testing results at the modal location. Likewise for soil series "a" the thickness to limiting layer was found to signficantly vary in a near northerly direction and a soil variation transect and soil property isotherm was established.

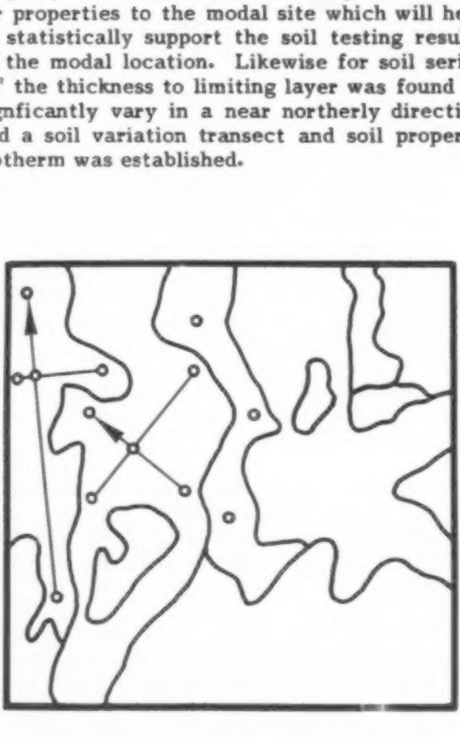


Figure 7. Detailed survey with transects and isotherms.

This example demonstrates how helpful the integration of site assessment information into the soil testing program can be and its important practical significance, as the total number of tests could be dramatically reduced (from 36 in Figure 4 to 13 tests in Figure 7) with the location of the actual testing sites established according to soil variation. Such a procedure would be a vast improvement over trying to grid a site to obtain an "average" hydraulic conductivity for a whole site.

Returning to the abc equation and the above discussion, it can be seen that using a soil series basis for "c" unit of land areas would be an improvement over use of some arbitrary land area such as acre or hectare because such a procedure would allow for less tests on a more uniform site and require more tests on sites that contain several soil series. Further, use of the soil series basis will allow the utilization of the vast amount of soils information that is already available in this form from the USDA which presently has data on approximately 12,000 soil series. Also, use of this type of terminology will allow for national consistency and also fit well with the approaches taken by other nations.

Considering the "b" types of tests part of the equation, it appears that attempts such as the Soil Testing Methods Matrix are beginning to provide answers to this problem even to the extent of assessing which types of tests are most applicable to the three categories of water movement that arise from the various types of land-based waste disposal.

Lastly, the "a" number of tests part of the abc equation remains the most unclear due to the paucity of available information regarding inherent variation of the testing methods as well as capabilities to quantitatively assess field soil spatial variability of hydrologic properties important in waste disposal. However, if done as suggested above with transects and isotherms, soil testing information from existing and newly proposed sites can be a valuable aid to research results that can accelerate the pace toward resolving the "a" number of "b" types of tests and establishing an abc equation that could be used on a uniform basis nationally for any type of land-based waste disposal site.

REFERENCES

1. ASTM Committee D-18. 1979. Standard Test Method for Infiltration Rate of Soils Using Double-Ring Infiltrometers, ASTM D 3385-75. Annual Book of ASTM Standards, Part 19.

2. Bertrand, A. R. 1965. Rate of Water Intake in the Field. In: Methods of Soil Analysis. C. A. Black, Ed. Amer. Soc. of Agronomy, Madison, Wisconsin. pp. 197-208.

3. Black, T. A., W. R. Gardner, and G. W. Thurtell. 1969. The Prediction of Evaporation, Drainage, and Soil Water Storage for a Bare Soil. Soil Sci. Soc. Amer. Proc. 33: 655-660.

4. Boersma, L. 1965a. Field Measurement of Hydraulic Conductivity Below A Water Table. In: Methods of Soil Analysis, C. A. Black, Ed. Amer. Soc. of Agronomy, Madison, Wisconsin. pp. 222-233.

5. Boersma, L. 1965b. Field Measurement of Hydraulic Conductivity Above A Water Table. In: Methods of Soil Analysis, C. A. Black, Ed. Amer. Soc. of Agronomy, Madison, Wisconsin. pp. 234-252.

6. Bouma, J., A. Jongerius, and D. Schoonderbeek. 1979. Calculation of Saturated Hydraulic Conductivity of Some Pedal Clay Soils Using Micromorphometric Data. Soil Sci. Soc. Amer. J. 43: 261-264.

7. Brewer, R. 1976. Fabric and Mineral Analysis of Soils. R. E. Krieger Publishing Co., Huntington, N. Y. 482 pp.

8. Childs, E. C. and N. Collis-George. 1950. The Permeability of Porous Materials. Roy. Soc. (London), Proc., A. 201: 392-405.

9. Davidson, J. M., L. R. Stone, D. R. Nielsen, and M. E. LaRue. 1969. Field Measurement and Use of Soil-Water Properties. Water Resources Res. 5: 1312-1321.

10. Flocker, W. J., M. Yamaguchi, and D. R. Nielsen. 1968. Capillary Conductivity and Soil Water Diffusivity Values from Vertical Soil Columns., Agron. J. 60: 605-610.

11. Gardner, W. R. 1970. Field Measurement of Soil Water Diffusivity. Soil Sci. Soc. Amer. Proc. 34: 832-833.

12. Gillham, R. W., A. Klute, and D. F. Heermann. 1976. Hydraulic Properties of a Porous Medium: Measurement and Empirical Representation. Soil Sci. Soc. Amer. J. 40: 203-207.

13. Hillel, D. and W. R. Gardner. 1970. Measurement of Unsaturated Conductivity and Diffusivity by Infiltration through an Impeding Layer. Soil Sci. 109: 149-153.

14. Jezequel, J. F. and C. Mieussens. 1975. In Situ Measurement of Coefficients of Permeability and Consolidation in Fine Soils. In: Proceedings of the Conference on In Situ Measurement of Soil Properties, A. S. C. E., New York, N. Y., Vol. I., pp. 208-224.

15. Klute, A. 1965a. Laboratory Measurement of Hydraulic Conductivity of Saturated Soil. In: Methods of Soil Analysis, C.A. Black, Ed. Amer. Soc. of Agronomy, Madison, Wisconsin. pp. 210-220.

16. Klute, A. 1965b. Laboratory Measurement of Hydraulic Conductivity of Unsaturated Soil. In: Methods of Soil Analysis. C. A. Black, Ed. Amer. Soc. of Agronomy, Madison, Wisconsin. pp. 253-261.

17. Klute, A. 1965c. Water Diffusivity. In: Methods of Soil Analysis, C. A. Black, Ed. Amer. Soc. of Agronomy, Madison, Wisconsin. pp. 262-272.

18. Klute, A. 1972. The Determination of the Hydraulic Conductivity of Unsaturated Soils. Soil Sci. 113: 264-276.

19. Lambe, T. W. and R. V. Whitman. 1979. Soil Mechanics, SI Version. John Wiley and Sons, New York, N. Y. 553 pp.

20. Libardi, P. L., K. Reichardt, D. R. Nielsen, and J. W. Biggar. 1980. Simple Field Methods for Estimating Soil Hydraulic Conductivity. Soil Sci. Soc. Amer. J. 44: 3-7.

21. Marshall, T. J. 1958. A Relation Between Permeability and Size Distribution of Pores. J. Soil Sci. 9: 1-8.

22. Matrecon, Inc. 1980. Lining of Waste Impoundment and Disposal Facilities Manual (Draft). U. S. Environmental Protection Agency, Cincinnati, Ohio. 595 pp.

23. Matyas, E. L. 1967. Air and Water Permeability of Compacted Soils. In: Permeability and Capillarity of Soils, ASTM STP 417, Amer. Soc. of Testing Materials. pp. 160-175.

24. Means, R. E. and J. V. Parcher. 1963. Physical Properties of Soils. Charles E. Merrill Books Inc., Columbus, Ohio. 464 pp.

25. Milligan, V. 1975. Field Measurement of Permeability in Soil and Rock. In: Proceedings of the Conference on In-Situ Measurement of Soil Properties, Vol. II, Specialty Conference of the Geotechnical Div., A.S.C.E., N. Carolina State University, Raleigh, North Carolina. pp. 3-36.

26. Millington, R. J. and J. P. Quirk. 1960. Transport in Porous Media. Trans. of 7th Int. Congr. Soil Sci., Madison, Wisconsin, I: 97-106.

27. Millington, R. J. and J. P. Quirk. 1961. Permeability of Porous Solids. Trans. Faraday Soc. 57: 1200-1207.

28. Millington, R. J. and J. P. Quirk. 1964. Formation Factor and Permeability Equations. Nature 202: 143-145.

29. Mitchell, J. K. 1976. Fundamentals of Soil Behavior. John Wiley and Sons, Inc., New York, N. Y. 422 pp.

30. Nielsen, D. R., J. M. Davidson, J. W. Biggar, and R. J. Miller. 1962. Water Movement through Panoche Clay Loam Soil. Hilgardia 35: 491-506.

31. Olson, R. E. and D. E. Daniel. 1979. Field and Laboratory Measurement of the Permeability of Saturated and Partially Saturated Fine-Grained Soils. Geotechnical Eng. Rep. GE 79-1, Dept. of Civil Eng., Univ. of Texas, Austin. 78 pp.

32. Roberts, D.W. and M.A. Nichols. 1980. Soil Properties, Classification, and Hydraulic Conductivity Testing (Draft). U.S. Environmental Protection Agency, Cincinnati, OH. 235 pp.

33. Simmons, C. S., D. R. Nielsen, and J. W. Biggar. 1979. Scaling of Field-Measured Soil-Water Properties. I. Methodology, II. Hydraulic Conductivity and Flux. Hilgardia 47: 77-153.

34. Small Scale Waste Management Project (SSWMP). 1978. Management of Small Waste Flows. EPA-600/2-78-173, U. S. Environmental Protection Agency, Cincinnati, Ohio. 764 pp.

35. Tzimas, E. 1979. The Measurement of Soil-Water Hysteretic Relationships on a Soil Monolith. J. Soil Sci. 30: 529-534.

36. Watson, K.K. 1966. An Instantaneous Profile Method for Determining the Hydraulic Conductivity of Unsaturated Porous Materials. Water Resources Res. 2: 709-715.

37. Yong, R. N. and B. P. Warkentin. 1975. Soil Properties and Behaviour. Elsevier Scientific Publishing Co., New York, N.Y. 449 pp.

EVALUATION OF MOLECULAR MODELLING TECHNIQUES TO ESTIMATE THE MOBILITY OF ORGANIC CHEMICALS IN SOILS:
II. Water Solubility and the Molecular Fragment Mobility Coefficient

James Dragun
U.S. Environmental Protection Agency
Washington, DC 20460

Charles S. Helling
U.S. Department of Agriculture
Beltsville, MD 20705

ABSTRACT

This is the second in a series of studies evaluating the use of various molecular modelling techniques to estimate the mobility of organic chemicals in soils. The objectives of this study were to (a) identify molecular fragments within organic chemicals that may significantly enhance or retard mobility in soils, (b) identify fragments that do not significantly enhance or retard mobility, (c) quantify the fragment effects and (d) incorporate these effects into the estimation method that predicted mobility from the logarithm of the solubility. Soil thin-layer chromatography was used to quantify the mobility of 55 pesticides, having diverse chemical structures, in Hagerstown silty clay loam soil. Thirteen fragments were identified and divided into two groups. One group of fragments possessed an electronegative or electropositive character whose mobility enhancement or retardation effects were not created by, or were negligibly affected by, aromatic ring resonance. In the second group, ring resonance played an important role in establishing mobility effects. Two least squares multiple regression models, incorporating water solubility and quantifying the surface repulsion or attraction effect as a molecular fragment mobility coefficient, successfully predicted R_f ($R^2 = 0.93$ and 0.94). These two models were superior techniques for predicting the mobility of diverse organic chemicals compared to the estimation technique utilizing solubility as the only independent variable.

INTRODUCTION

Knowledge concerning the potential adsorption of organic chemicals to sediments and soils is essential for assessing the hazard to human health and the environment associated with various wastewater, sludge and chemical use and disposal methods. The degree of adsorption will affect the mobility of a chemical as well as other fate determining processes such as volatilization, photolysis, hydrolysis and biodegradation. Legislation such as the Federal Water Pollution Control Act and its Amendments (FWPCA), the Toxic Substances Control Act (TSCA), the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), the Resource Conservation and Recovery Act (RCRA) has created a need for adsorption and mobility data.

The most widely used and accepted estimation techniques to predict the extent of adsorption involve correlation of the solid-to-solution distribution coefficient (K_d) or the retention factor (R_f), derived from soil thin-layer chromatography (TLC), to some measure of the molecular hydrophobicity. The measure usually chosen is the logarithm of the solubility (log S) [Karickhoff et al. (14); Dragun et al. (3)] or the logarithm of the octanol:water partition coefficient (log P) [Briggs (2); Dragun et al. (3); Karickhoff et al. (14)]. However, these estimation techniques usually provide only general approximations of the mobility of a chemical in soil or the potential for adsorption to sediments. For example, when K_{OC} (i.e., the adsorption coefficient divided by the fractional organic carbon content present in the soil or sediment) versus solubility was plotted [Mill and Mabey (16)] using data from three sources, the predicted values of K_{OC} varied from observed values by at least one order of magnitude for 20 of the approximately 100 chemicals, and by at least two orders of magnitude for 3 chemicals.

While organic chemical mobility is mainly governed by its lipophilic attraction to soil organic matter, it is affected to some extent by electrical charge phenomena. Recent reviews [Harter (8); Theng (21)] have implicated the type and amount of clay, the exchange capacity and surface acidity as factors affecting the extent of adsorption. Dragun et al. (3), using molecular connectivity indices and molecular charge transfer calculations, concluded that size and shape of the molecules and molecular polarization induced by clay particle charge fields appear to be of negligible importance compared to the hydrophobic-hydrophilic balance of the molecule for mobility prediction purposes. However, this study also suggested that future attempts to model chemical mobility in soils should consider the interaction of molecular fragments with colloid surfaces bearing permanent and pH-dependent charge. The attractive and repulsive interactions of various molecular fragments with colloid surfaces has been studied [Mortland (17, 18); Tahoun and Mortland (20); Theng (21)]. However, no attempt has been made to quantify these molecular fragment interactions into a mobility estimation technique. The purposes of this study were to identify the mobility enhancement and retardation effects of various molecular fragments and to quantitatively incorporate these effects into an existing estimation technique based on solubility. This report is the second in a series of studies evaluating the use of various modelling techniques to estimate the mobility of organic chemicals in soils.

THEORETICAL DISCUSSION

Hammett (6) related the rate constant of a meta or para substituted derivative of C_6H_5-X (with X as the reacting center) to the parent structure using the general relationship (the Hammett equation):

$$\log (k_s/k_0) = \rho\sigma \qquad [1]$$

The quantity k_0 represents the rate constant of the unsubstituted parent structure and k_s that of the substituted derivative. The quantity σ is a Gibbs energy related fragment or substituent constant that reflects the ability of the fragment to attract or repel electrons and ρ is a constant characteristic of the type of reaction. By analogy with the Hammett equation, Hansch and Leo (7) described lipophilicity as:

$$\log [P_{RX}/P_{RH}] = \rho\pi(x) \qquad [2]$$

where P_{RH} and P_{RX} represent the solvent-solvent partition coefficients of the organic molecule R containing H and X fragments; $\pi(x)$ represents the hydrophobic fragment constant, i.e., the contribution of substituent X to the lipophilicity of the structure RH when X replaces a hydrogen atom in RH; and ρ reflects the characteristics of the solvent pair used in determining the partition coefficient. The constant π is a Gibbs energy related constant which measures the difference in the Gibbs energy changes involved in moving RH and RX from one solvent phase to another. The practical applications of Equation 2 are significant. For any structure R, the total lipophilicity as measured in an octanol:water system can be construed by simple addition of the proper π values characterizing the fragments [Hansch and Leo (7)]:

$$\log P_R = \sum_n \pi(x_n) \qquad [3]$$

where n is the total number of fragments comprising the structure R. Dragun et al. (3) showed that R_f values >0.1 can be represented as a linear function of log S, which in turn is linearly related to log P_R. Therefore, R_f can be defined in terms of π or log S for the structure R:

$$R_f = a \sum_n \pi(x_n) + b \qquad [4]$$

or alternatively by

$$R_f = c \log S + e \qquad [5]$$

where a, b, c, and e are constants. By analogy with σ of Equation 1, the quantity ∂ can be defined as the substituent or fragment coefficient that reflects the Gibbs energy effects caused by attraction to or repulsion from colloid surface charges, thereby retarding or enhancing mobility (i.e., the molecular fragment mobility coefficient). We assumed that the magnitude of a fragment's mobility enhancing or retarding effect was a constant, independent of the structure of the parent molecule. An analysis of the sediment adsorption data of Hassett et al. (9) for the primary amine fragment of various polynuclear aromatic amines indicates that these two assumptions appear reasonable. We also assumed that, for an organic chemical RX having the fragment X that interacts with soil colloid surfaces, the ∂ values are independent of, and additive with, the π values. Then, R_f can be defined in terms of ∂ and π or log S:

$$R_f = a \sum_n \pi(x_n) + \rho\partial + b \qquad [6]$$

or

$$R_f = c \log S + \rho\partial + e \qquad [7]$$

The quantity ρ is a constant characteristic of the soil system. The objectives of this study were to (a) identify molecular fragments that may significantly enhance or retard organic chemical mobility in soils, (b) identify fragments that do not significantly enhance or retard mobility, (c) quantify ∂ for fragments identified in (a) above, and (d) incorporate ∂ into the log S - R_f relationship to provide an improved approach for estimating the mobility of organic chemicals in soils.

MATERIALS AND METHODS

Soil Mobility Determination

Soil TLC is a laboratory method using soil as the adsorbent phase in a TLC system. By its innate homogeneity, the adsorbent in TLC represents the milieu of a chemical moving through soil aggregates rather than around them. This relatively simple system yields quantitative data on the mobility of organic chemicals that correlate well with trends noted in the literature on field tests and monitoring studies. Soil TLC [Helling (10)] was used as the basis for quantifying the mobility of organic chemicals used in this study. R_f values for most of these chemicals on Hagerstown silty clay loam soil have been previously reported [Helling (10); Helling et al. (11, 12)]. R_f values for norflurazon and perfluidone were determined on Hagerstown silty clay loam soil by the same method used for the other chemicals. A standard development distance, 100 mm, was used on all plates. The R_f is obtained directly by measuring the distance the chemical migrates in mm on the plate and dividing this distance by 100 mm (e.g., 70 mm = R_f of 0.70). Table 1 contains the common and chemical names and the R_f values of the 55 organic chemicals used in this study.

The soil contained 2.50% organic matter and 39.5% clay. The soil pH was 6.8. Moisture capacity at a pressure of 33 kPa (1/3 bar) was 34.1% for soil sieved to less than 250 µm. The dominant clay minerals were vermiculite and kaolinite.

Solubility Determinations

The water solubilities of the 55 organic chemicals used herein were obtained from the literature and are listed in Table 1.

Molecular Fragment Selection and Analysis

The organic chemicals selected for this study have diverse chemical structures, thereby allowing the analysis of the mobility enhancement or retardation effects of a large number of molecular fragments. Most of these chemicals are polyfunctional, i.e., they contain more than one fragment or substituent group. However, using the assumptions and methods described in this section, most chemicals were found to be monofunctional with respect to mobility enhancement or retardation, even though they were polyfunctional in structure. First, the least squares linear regression of solubility on R_f was calculated:

$$R_f = 0.20 \log S + 0.03; \quad (R^2 = 0.50) \qquad [8]$$

Then, all organic chemicals containing an aromatic fragment were plotted in relation to Equation 8 (in a manner analogous to Figure 1). Aliphatic chemicals were not treated in this analysis using Equation 8 for reasons that are discussed in the Results and Discussion section. Chemicals containing a given fragment were identified

TABLE 1. COMMON AND CHEMICAL NAMES, R_f AND THE LOG OF THE SOLUBILITY IN PPM (log S) OF CHEMICALS USED IN THIS STUDY

No.	Common Name	Chemical Name	R_f	log S [a]
1.	Ametryne	2-(ethylamino)-4-(isopropylamino)-6-(methylthio)-*s*-triazine	0.44	2.27
2.	Amiben	3-amino-2,5-dichlorobenzoic acid	0.91	2.85
3.	Amitrole	3-amino-*s*-triazole	0.73	5.45
4.	Atratone	2-ethylamino-4-isopropylamino-6-methoxy-*s*-triazine	0.56	3.22
5.	Atrazine	2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine	0.47	1.52
6.	Aziprotryne	2-azido-4-(isopropylamino)-6-(methylthio)-*s*-triazine	0.30	1.88
7.	Barban	4-chloro-2-butynyl *m*-chlorocarbanilate	0.04	1.04
8.	Bromacil	5-bromo-3-*sec*-butyl-6-methyluracil	0.49	2.91
9.	Captan	*N*-[(trichloromethyl)-thio]-4-cyclohexene-1,2-dicarboximide	0.19	-0.30
10.	Carbaryl	1-naphthyl methylcarbamate	0.38	1.60[b]
11.	CDAA	*N*,*N*-diallyl-2-chloroacetamide	0.82	4.30[a]
12.	Chlorbromuron	3-(4-bromo-3-chlorophenyl)-1-methoxy-1-methylurea	0.14	1.70
13.	Chloroxuron	3-[*p*-(*p*-chlorophenoxy)-phenyl]-1,1-dimethylurea	0.09	0.57
14.	Chlorpropham (CIPC)	isopropyl *m*-chlorocarbanilate	0.18	1.95
15.	Cycloheximide	3-[2-(3,5-dimethyl-2-oxocyclohexyl)-2-hydroxyethyl] glutarimide	0.88	4.32[a]
16.	2,4-D	2,4-dichlorophenoxyacetic acid	0.69	2.78
17.	Dalapon	2,2-dichloropropionic acid	0.96	5.70
18.	Dicamba	3,6-dichloro-*o*-anisic acid	0.96	3.65
19.	Dichlobenil	2,6-dichlorobenzonitrile	0.22	1.26
20.	Diphenamid	*N*,*N*-dimethyl-2,2-diphenylacetamide	0.49	2.41
21.	Diuron	3-(3,4-dichlorophenyl)-1,1-dimethylurea	0.24	1.62

No.	Common Name	Chemical Name	R_f	log S [a]
22.	Fenac	2,3,6-trichlorophenylacetic acid	0.84	2.30
23.	Fenaminosulf (Dexon)	p-(dimethylamino)-benzenediazo sodium sulfonate	0.08	4.48
24.	Fenuron	1,1-dimethyl-3-phenylurea	0.69	3.59
25.	Fluometuron	1,1-dimethyl-3-(alpha,alpha,alpha-trifluoro-m-tolyl)urea	0.50	1.90
26.	Formetanate Hydrochloride	m-[[(dimethylamino)-methylene]amino]-phenyl methylcarbamate hydrochloride	0.75	3.00
27.	Linuron	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea	0.17	1.88
28.	MCPA	2-chloro-4-methyl phenoxyacetic acid	0.79	2.95
29.	Metobromuron	3-(p-bromophenyl)-1-methoxy-1-methylurea	0.31	2.52
30.	Monuron	3-(p-chlorophenyl)-1,1-dimethylurea	0.48	2.36
31.	Neburon	1-butyl-3-(3,4-dichlorophenyl)-1-methylurea	0.07	0.68
32.	Norflurazon	4-chloro-5-(methylamino-2-(3-trifluoromethyl-phenyl)pyridazin-3-one	0.40	1.45
33.	Nortron	6-chloro-2-trifluoromethyl-3H-imidazo-[4,5-b]pyridine]	0.65	2.04
34.	Oxycarboxin	5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide 4,4-dioxide	0.73	3.00
35.	PCP	pentachlorophenol	0.40	1.30[b]
36.	Perfluidone	1,1,1-trifluoro-N-[2-methyl-4-(phenylsulfonyl)-phenyl]-methane-sulfonamide	0.82	1.78[c]
37.	Phenmedipham	methyl m-hydroxycarbanilate m-methylcarbanilate	0.17	1.00
38.	Picloram	4-amino-3,5,6-trichloropicolinic acid	0.84	2.63
39.	PPG - 124	p-chlorophenyl methylcarbamate	0.57	2.76[a]

No.	Common Name	Chemical Name	R_f	log S [a]
40.	Promecarb	3-isopropyl-5-methyl phenyl methylcarbamate	0.34	1.96
41.	Prometone	2,4-bis(isopropylamino)-6-methoxy-s-triazine	0.60	2.88
42.	Prometryn	2,4 bis(isopropylamino)-6-methylthio-s-triazine	0.25	1.68
43.	Propachlor	2-chloro-N-isopropyl-acetanilide	0.63	2.85
44.	Propanil	3',4'-dichloropropionanilide	0.24	2.35
45.	Propazine	2-chloro-4,6-bis(isopropylamino)-s-triazine	0.41	0.93
46.	Propham	isopropyl carbanilate	0.51	2.10
47.	Pyrazon	5-amino-4-chloro-2-phenyl-3(2H)-pyridazinone	0.44	2.60
48.	Siduron	1-(2-methylcyclohexyl)-3-phenylurea	0.30	1.26
49.	Simazine	2-chloro-4,6-bis(ethylamino)-s-triazine	0.45	0.70
50.	Simetone	2,4-bis(ethylamino)-6-methoxy-s-triazine	0.45	3.51
51.	Simetryn	2,4-bis(ethylamino)-6-(methylthio)-s-triazine	0.33	2.65
52.	Solan	3'-chloro-2-methyl-p-valerotoluidide	0.08	0.95
53.	2,4,5-T	2,4,5-trichlorophenoxyacetic acid	0.54	2.38
54.	TCA	trichloroacetic acid	0.90	6.08
55.	Trietazine	2-chloro-4-diethylamino-6-ethylamino-s-triazine	0.38	1.30

---

[a] From the Pesticide Manual, British Crop Protection Council (1974) at 20-25 C, unless specified otherwise.

[b] Measured at 30°C.

[c] From Thomson WT, Agricultural Chemicals Review, 1979 Revision, Thomson Publications, Fresno, CA.

[d] Measured at 3°C.

[e] From Herbicide Handbook, Weed Science Soc. America (1974).

on the plot in relation to Equation 8. The distribution of the fragment was then classified using inductive reasoning as either (a) mobility enhancing (i.e., most chemicals with a given fragment, when plotted in relation to Equation 8, appeared to the left of regression line), (b) mobility retarding (i.e., most chemicals appeared to the right of the regression line) or (c) no observable effect. Karickhoff et al. (14) showed that mono-, di- and polycyclic aromatic hydrocarbon and chlorinated hydrocarbon adsorption is highly correlated to solubility. This study assumed that R_f is highly correlated with water solubility for unsubstituted aliphatic and aromatic hydrocarbons. Therefore, aliphatic and aromatic hydrocarbon fragments were classified as having a statistically nonsignificant effect. An analysis of the distribution of these fragments shows that this classification, in general, was valid for the chemicals used in this study. The results of these fragment plots were quantified and statistically analyzed by developing the linear least squares fit model that was analogous to Equation 7:

$$R_f = m \log S + b\lambda_1 + c\lambda_2 + \cdots + d\lambda_n + e \qquad [9]$$

where

e, m = constants
S = water solubility in ppm
λ_1, λ_2, λ_n = molecular fragment mobility coefficients
b, c, d = unity, if the molecule contains the fragment that is classified as mobility enhancing or retarding
or b, c, d = zero, if the fragment is not classified as mobility enhancing or retarding (i.e., fragment has no observable effect), or if the fragment is not present within the molecule.

The quantity a, derived in Equation 7, was assigned a value of unity and is, therefore, not found in Equation 9.

Since the slope and intercept of Equation 9 were somewhat different than those of Equation 8, all organic chemicals containing an aromatic fragment were replotted, but in relation to Equation 9 with the values b, c and d equal to zero. Chemicals containing a given fragment were again identified on the plot, but in relation to the modified version of Equation 9. The fragment was then reclassified using inductive reasoning as either mobility enhancing, mobility retarding or no effect. Then, the λ values were reestimated for those fragments that either enhanced or retarded mobility through the development of a new linear least squares fit model similar to Equation 9. This iterative reestimation of the λ values was repeated three times. On the third iteration, no new fragments were identified and no fragment changed its mobility class.

RESULTS AND DISCUSSION

Aliphatic Chemicals

Figure 1 shows the graphical relationship between R_f and log S for the organic chemicals used in this study. Two distinct relationships exist between R_f and log S: one R_f - log S relationship fits chemicals containing no aromatic fragments (i.e., aliphatics) and one fits chemicals containing at least one aromatic fragment (i.e., aromatics). Since soil organic matter contains both aliphatic and aromatic constituents, the strength of chemical binding to soil may be influenced by the inherent aliphatic or aromatic character of the chemical. Therefore, these two distinct groups were treated separately in this study. This observation also suggests that future attempts to model mobility should distinguish aliphatic from aromatic chemicals.

Six organic chemicals comprise the aliphatics group. Each of these contains at least one of three molecular fragments that possibly interact with colloid surfaces [Hamaker (8); Mortland (17)]: the carbonyl, the primary amine, and the carboxylic acid group. Three chemicals contained one of these fragments (No. 11, 17, 58), two contained two molecular fragments (No. 8, 9), and one contained three fragments (No. 15). Since each of the chemicals contained at least one fragment that may interact with colloid surfaces, λ values were not calculated.

Aromatic Chemicals

Table 2 identified the molecular fragments that did not enhance or retard the

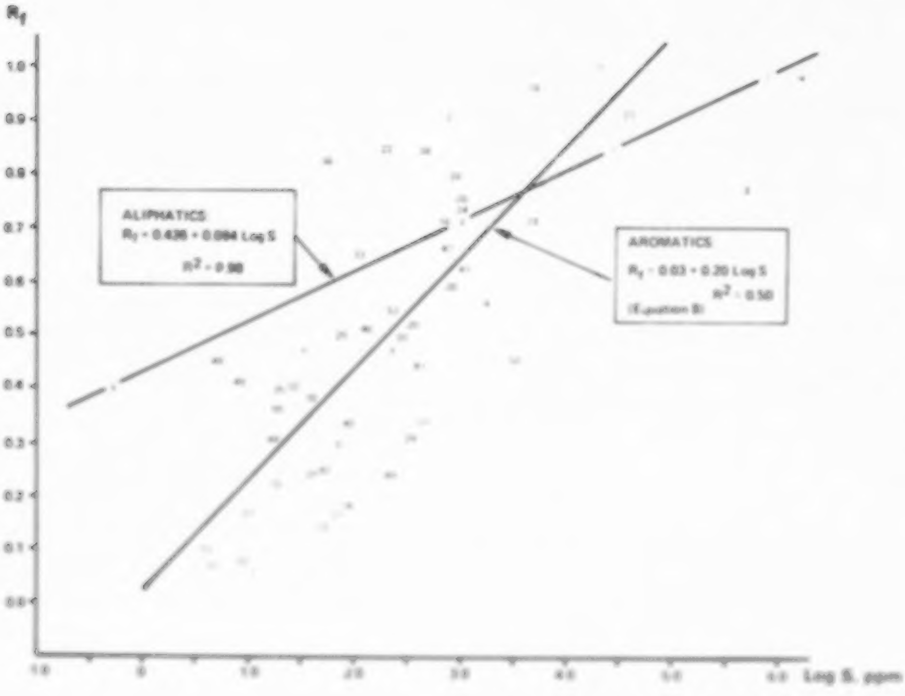


Figure 1. Linear relationships between the logarithm of water solubility (log S; ppm) and the soil TLC R_f for 7 aliphatic and 48 aromatic organic chemicals.

mobility of these organic chemicals beyond the limits of statistical nonsignificance and the number of aromatic chemicals containing the fragment. One classic view of the adsorption of polar but nonionic organic molecules by clay minerals attributes a major portion of the surface interaction to functional groups containing nitrogen and oxygen [Harter [8]; Mortland [17]; Theng [21]]. In this study, however, most of the fragments listed in Table 2 that apparently did not enhance or retard mobility contained either nitrogen or oxygen or both. Apparently the interaction is insignificant for these fragments compared to the molecule's hydrophobicity, for soil mobility prediction purposes. So far as we are aware, a significant interaction of chlorinated alkyl and aryl chemicals with colloid surfaces, except for the findings of Briggs [1], has not been reported. The findings of this study, in general, do not provide evidence for the existence of the interaction.

Table 3 lists those molecular fragments that either enhanced or retarded the soil mobility of aromatic chemicals. Regression Model I, based on Equation 9, was developed:

$$R_f = 0.208 \log S + 0.003 + b_1 \qquad [10]$$

where b_1 is the molecular fragment mobility coefficient ($R^2 = 0.92$). Model II was then derived from Model I:

$$\log [R_f/(1 - R_f)] = 0.888 \log S - 1.131 + b_2 \qquad [11]$$

where b_2 is the molecular fragment mobility coefficient. It was fitted to the logit transformation of the observed chemical mobility in order to constrain the predicted response to values between zero and unity ($R^2 = 0.84$). The quantities b_1 and b_2 are assigned values of zero for any fragment that is not listed in Table 3. If the fragment is listed, b_1 or b_2 is assigned

TABLE 2. MOLECULAR FRAGMENTS THAT NEITHER ENHANCED NOR RETARDED SOIL MOBILITY OF VARIOUS AROMATIC CHEMICALS

Fragment	Number of chemicals
Amide, substituted	5
Amine, secondary	14
" tertiary*	5
Azide	1
Carbamate	8
Cyanide	1
Diazosulfonate	1
Ether	5
Halogen, alkyl	4
" aryl†	24
Imine	2
Pyridazinone	2
Sulfone	1
Urea	10

*Includes the tertiary amine within the pyridazinone fragment.

†Exceptions noted in Table 3.

the corresponding value from Table 3. Both models only accommodate one fragment per molecule.

The molecular fragments listed in Table 3 can be divided into two groups. The first group is comprised of those fragments that possess an electropositive or electronegative character that is not created by, or is negligibly affected by, aromatic ring resonance. Since Hagerstown soil colloid surfaces possess a net negative charge, fragments that possess an electronegative character should be repelled from these colloid surfaces [Greenland (4); Mortland (17)]. Mobility enhancement of the molecule in this soil should result. The β values of Table 3 showed the the carboxyl, trifluoromethyl and trifluoromethylsulfonyl fragments enhanced soil chemical mobility, in agreement with this hypothesis. At soil pH 6.8, the dissociated carboxylic acid fragment, possessing a negative charge, was assumed to be minimally affected by resonance. However, this assumption will not be valid

TABLE 3. MOLECULAR FRAGMENTS ENHANCING (+) OR RETARDING (-) MOBILITY OF AROMATIC CHEMICALS, AND THEIR MOBILITY COEFFICIENTS (β)*

Fragment	β_1†	β_2§	Chemical
Acid, carboxylic			
benzoic	0.23	0.70	19
benzylic	0.36	0.77	22
phenoxyacetic	0.17**	0.18**	16, 28, 53
Amine, aliphatic, primary	-0.13**	-0.19	47
Benzene			
p-bromo	-0.22	-0.61	29
m-chloro	-0.19	-0.53	7, 18
m,p-dihalo	-0.17	-0.70	12, 21, 27, 31, 48
hydroxy (dissociated)	0.12**	0.35	35
Triazine			
chloro	0.19	0.67	5, 40, 49, 55
methoxy	-0.13	-0.31	8, 51, 59
methylthio	-0.12	-0.20	1, 8, 52, 51
Trifluoromethyl	0.16	0.32	25, 32, 33
Trifluoromethylsulfonyl	0.45	0.86	36

*Values are significant at or below 5% level, except those (**) at 10% level.

†Used in Model I (Equation [3]).

§Used in Model II (Equation [2]).

at low soil pH's. Fragments that possess a permanent or pH-dependent electropositive character should be attracted to Hagerstown soil colloid surfaces [Mortland (17); Theng (21)] and mobility retardation of the molecule should result. Table 3 also showed that this was the case for the aliphatic primary amine fragment, which possesses a pH-dependent electropositive character.

The second group of molecular fragments listed in Table 3 includes those in which resonance is significant. It contains three subgroups. The s-triazine subgroup chemicals share a common ring structure and possess similar amino fragments. The general properties and reactions of the s-triazines, and hence the behavior of these compounds at the clay surface, are related to the nature and location of the ring substituent groups. Weber (22) concluded that the adsorption process is primarily controlled by the nature of the non-amino fragment. In this study, mobility enhancement or retardation effects were primarily due to non-amino fragments. The chloro fragment significantly enhanced mobility, probably through surface repulsion due to its mild electron withdrawing effect, while the methoxy and methylthio fragments retarded mobility. These findings agree, in general, with other studies dealing with the relative ranking of the clay adsorption potential of similar s-triazines [Theng (21)].

The halogen-substituted benzenes comprise the second subgroup within the resonance group of molecular fragments. This subgroup is composed of carbanilates, phenylureas and an anilide. Significant retardation of mobility was observed with chlorine substitution in the 3 (meta) position. Bromine, chlorine or methyl substitution in the 4 (para) position did not alter the retardation effect of 3-chloro fragment; however, additional ring substitutions, in general, destroyed the retardation effect. Significant retardation of mobility was observed for bromine substitution in the para position with only one chemical (No. 28). Briggs (3) found similar significant changes in adsorption due to chlorination of n-alkyl phenylureas at the meta position and reported that the best linear relationship with the adsorption distribution coefficient was obtained by using the Hammett sigma constant for meta and para substituents in the phenyl ring. However, two assumptions made in this study were that the magnitude of a fragment's mobility-enhancing or -retarding effect was (a) constant and (b) independent of the structure of the parent molecule. An examination of Figure 1 reveals that, in general, this was the case for the halogen substituted benzene subgroup (No's. 7, 12, 14, 21, 27, 29, 31, 44, 52). Some variance in Figure 1 can be atributed to the solubility data which were obtained from the literature and were not necessarily measured in the same laboratory under similar experimental conditions. Variance can also be attributed to the fact that at $R_f \leq 0.1$, the R_f - log S relationship is, in general, curvilinear. Due to these sources of variance, the study of the linear free energy relationships of this subgroup, as applied to Models I and II, appeared unwarranted and was therefore not attempted.

A unique chemical within the halogen substituted benzenes is PCP or pentachlorophenol (No. 35). Increasing the chlorine substitution around an aromatic ring results in decreasing pK_a. Since the pK_a of phenol is 9.89 and the pK_a of trichlorophenol is 6.00, the pK_a of PCP should be well below 6.00. Therefore, PCP is expected to exist as an anion with some degree of mobility enhancement caused by the dissociated hydroxyl group. The data in Table 3 show that this may have been the case. The use of these hydroxybenzene π values, however, should be applicable only to this special case.

The aromatic ring substituted primary amines are the third subgroup within the resonance group of molecular fragments (Nos. 2, 3, 38). Chemical 3's position in Figure 1 indicates that the primary amine fragment retards mobility. An analysis of the sediment adsorption data of Hassett et al. (9) for the primary amine fragment of various polynuclear aromatic hydrocarbons also indicates that the fragment should retard mobility and enhance adsorption. On the other hand, the position of chemicals No. 2 and 38 in Figure 1 indicates that this fragment enhances mobility. These two chemicals are chlorinated and contain a carboxylic acid fragment whose enhancement effect cannot be separated from the primary amine effect. Therefore, the π value for the primary amine fragment cannot be estimated with confidence using these data and these three chemicals were not included in the development of Models I and II.

Comparison of Models

Table 4 lists the difference, $\Delta R_f(\underline{8})$, between the observed R_f and the R_f predicted by Equation 8 (the model which utilized log S as the only independent variable) for 46 of the chemicals used in this study. Table 4 also lists the difference, $\Delta R_f(\underline{10})$ between the observed R_f and the R_f predicted by Model I (the model which utilized both log S and as independent variables). Relative to $\Delta R_f(\underline{8})$, the absolute values of $\Delta R_f(\underline{10})$ were lower for 32 chemicals, equal for 7 chemicals, and somewhat higher for 7 chemicals. Therefore, Model I was the superior model for predicting the soil mobility of these organic chemicals.

Soil adsorption and mobility estimation techniques may be used to assign a chemical to a general mobility class in order to approximate the distance a surface-applied chemical may leach. Another indication of the accuracy of a predictive technique is its ability to place a chemical into the observed mobility class. Helling and Turner (13) proposed five mobility classes: Class 1, R_f 0-0.09 (immobile); Class 2, R_f 0.10-0.34 (slightly mobile); Class 3, R_f 0.35-0.64 (intermediate mobility); Class 4, R_f 0.65-0.80 (mobile); and Class 5, R_f 0.90-1.00 (very mobile). Table 4 shows that the use of Equation 8 places 31 chemicals into the wrong mobility class. On the other hand, the use of Model I places only 7 chemicals in the wrong class, with 6 of these chemicals being on the borderline of the proper class. Compared to the estimation technique utilizing solubility as the only independent variable, we concluded that the estimation technique represented by Models I and II, utilizing both log S and the ∂ molecular fragment mobility coefficient as independent variables, is a superior technique for predicting the mobility of diverse organic chemicals in Hagerstown silty clay soil.

TABLE 4. DIFFERENCE BETWEEN OBSERVED R_f AND THAT PREDICTED BY EQUATIONS 8 [$\Delta R_f(\underline{8})$] OR 10 [$\Delta R_f(\underline{10})$], FOR 46 ORGANIC CHEMICALS

Chemical	$\Delta R_f(\underline{8})$	$\Delta R_f(\underline{10})$	Chemical	$\Delta R_f(\underline{8})$	$\Delta R_f(\underline{10})$
1	-0.04	0.08	31	-0.10*	0.10
4	-0.11*	0.02	32	0.08*	-0.04
5	0.14*	-0.04	33	0.21*	0.08*
6	-0.11*	0.02	34	0.10*	0.10*
7	-0.18*	0.03	35	0.11*	0.00
10	0.03	0.03	36	0.43*	0.00
12	-0.23*	-0.05	37	-0.06	-0.04
13	-0.09*	-0.03*	39	-0.01	-0.01
14	-0.28*	-0.04	40	-0.08*	-0.07*
16	0.10*	0.01	41	-0.01	0.13
18	0.29*	0.00	42	-0.12*	0.02
19	-0.06	-0.05	43	0.03	0.03
20	-0.02	-0.01	44	-0.26*	-0.09
21	-0.11*	0.07	45	0.19*	0.02
22	0.39*	0.00	46	0.06	0.07
23	-0.09*	-0.09*	47	-0.11	0.00
24	-0.06	-0.06	48	0.02	0.03
25	0.09	-0.04	49	0.29*	0.13
26	0.12*	0.12*	50	-0.29*	-0.15
27	-0.24*	-0.05	51	-0.23*	-0.13
28	0.17*	0.07	52	-0.18*	0.12*
29	-0.22*	0.00	53	0.03	0.08
30	-0.02	-0.01	55	0.07*	-0.13

*Predicted mobility class differed from the observed mobility class (classes were defined by Helling and Turner (13)).

DISCLAIMER

The contents and views expressed in this article do not necessarily reflect the views and policies of the U.S. Department of Agriculture or the Environmental Protection Agency, nor does the mention of trade names and commercial products constitute endorsement or recommendation for use.

REFERENCES

1. Briggs, G. G. 1969. Molecular structure of herbicides and their sorption by soils. Nature 223:1288.

2. Briggs, G. G. 1973. A simple relationship between soil adsorption of organic chemicals and their octanol-water partition coefficient. Proc. 7th Brit. Insectic. Fungic. Conf. 1:83-86.

3. Dragun, J., R. Potenzone, Jr., C. S. Fowler, and C. S. Helling. 1980. Evaluation of molecular modelling techniques to estimate soil-chemical mobility: I. Molecular connectivity and charge related indices. Proc. Res. Symp., 53rd Ann. Mtg., Water Pollut. Contr. Fed., Las Vegas, NV.

4. Greenland, D. J. 1965. Interaction between clays and organic compounds in soils. Part I. Mechanisms of interaction between clays and defined organic compounds. Soils Fert. 28:415-425.

5. Guth, J. A., N. Burkhard, and D. O. Eberle. 1976. Experimental models for studying the persistence of pesticides in soils. In: Proc. Brit. Crop Protect. Coun. Symp.: Persistence of Insecticides and Herbicides (K. I. Beynon, ed.), Monogr. No. 17, Brit. Crop Protect. Coun., pp. 137-157.

6. Hammett, L. P. 1940. Physical Organic Chemistry. McGraw-Hill, New York. 404 pp.

7. Hansch, C., and A. Leo. 1979. Substituent Constants for Correlation Analysis in Chemistry and Biology. Wiley, New York. 339 pp.

8. Harter, R. D. 1977. Reactions of minerals with organic compounds in the soil. In: Minerals in Soil Environments (J. B. Dixon and S. B. Weed, eds.). Soil Sci. Soc. Am., Inc., Madison, WI. pp. 709-739

9. Hassett, J. J., J. C. Means, W. L. Banwart, and S. G. Wood. 1980. Sorption Properties of Sediments and Energy-Related Pollutants. EPA 600/3-80-041, U.S. Environmental Protection Agency, Athens, GA. 133 pp.

10. Helling, C. S. 1971. Pesticide mobility in soils: I. Parameters of soil-thin layer chromatography. Soil Sci. Soc. Am. Proc. 35:732-737.

11. Helling, C. S., D. G. Dennison, and D. D. Kaufman. 1974. Fungicide movement in soils. Phytopathology 64:1091-1100

12. Helling, C. S., D. D. Kaufman, and C. T. Dieter. 1971. Algae bioassay detection of pesticide mobility in soils. Weed Sci. 19:685-690.

13. Helling, C. S., and B. C. Turner. 1968. Pesticide mobility: Determination by soil-thin layer chromatography Science 162:562-563.

14. Karickhoff, S. W., D. S. Brown, and T. A. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Res. 13:241-248.

15. Meyers, H. E. 1937. Physico-chemical reactions between organic and inorganic soil colloids as related to aggregate formation. Soil Sci. 44:331-357.

16. Mill, T., and W. R. Mabey. 1980. Laboratory Protocols for Evaluating the Fate of Organic Chemicals in Air and Water. Final Rep., Contract No. 68-03-2227, U.S. Environmental Protection Agency, Washington, DC. 329 pp.

17. Mortland, M. M. 1970. Clay-organic complexes and interactions. Adv. Agron. 75-117.

18. Mortland, M. M. 1972. Clay-organic complexes and interactions: aromatic molecules. Proc. IUPAC Symp. Environ. Qual. Safety 3:[illegible].

19. Rekker, R. F. 1977. The Hydrophobic Fragmental Constant, Vol. 1. Elsevier, New York. 389 pp.

20. Tahoun, S. A., and M. M. Mortland. 1966. Complexes of montmorillonite with primary, secondary and tertiary amides: 1. Protonation of amides on the surface of montnorillonite. Soil Sci. 102:248-254.

21. Theng, B. K. G. 1974. The Chemistry of Clay-Organic Reactions. Adam Hilger, London. 343 pp.

22. Weber, J. B. 1966. Molecular structure and pH effects on the adsorption of 13 *s*-triazine compounds on montmorillonite clay. Am. Mineral. 51:1657-1670.

PREDICTION OF LIACHATE PLUME MIGRATION

SHWRD Annual Research Symposium

Wayne A. Pettyjohn
Oklahoma State University
Stillwater, Oklahoma 74078

Douglas C. Kent
Oklahoma State University
Stillwater, Oklahoma 74078

Thomas A. Prickett
Consultant
Champaign, Illinois 61820

Harry E. LeGrand
Consultant
Raleigh, North Carolina 27609

ASTRACT

The purpose of this investigation is to develop a manual for predicting leachate plume migration and mixing in ground water that is typified by concepts and techniques that will prove useful to a permit writer with littl or no expertise in hydrology. The general approach is the development of a series oftechniques, ranging from very simple to rather complex that take into account the chemica and physical factors that control or influence chemical transport. The broad range of techniques consists of three phases--a numerical rating system, analytical-graphical solutions, and computer models.

Introduction

The purpose of this study is to develop a manual that will serve as a guide to U.S. Environmental Protection Agency permit writers in evaluating permit applications dealing with hazardous waste storage, treatment, and disposal facilities, as describe in Section 3004 of the Resource Conservation and Recovery Act. This investigation, only one of several under development, is designed generally for predicting leachate mixing and movement in ground water and specifically addresses three major questions.

1. How much will leachate constituent concentrations be reduced by mixing with ground water?
2. In what direction will the leachate plume travel and how will its shape change along the travel path?
3. Which ground-water models are appropriate for predicting movement of solutes in ground water at a site with specific hydrogeologic characteristics, assuming that the solutes do not interact with aquifer materials?

It is assumed that the permit applicants will use a variety of methods for predicting effects of a disposal site on ground water and that the permit writer will not have a strong background in hydrology. Consequently, the manual will provide a variety of predictive techniques that range from exceedingly simple to highly complex, all of which are based on sound hydrogeological principles, but which are presented in a simplified manner. The project is conceived as consisting of two separate parts continuing through a time frame of three years. During the first year prediction techniques will be developed and tested using available data. During the second two years the models will be applied to several existing sites that are located throughout the nation and represent the broadest range of hydrogeologic environments that can be obtained within the limits of time and funding.

Fundamentals of Ground-Water Flow

From a hydrogeologic point of view, the subsurface is divided into two distinct zones--(1) the unsaturated zone, which extends from land surface to some depth where the water table is encountered, and (2) the saturated zone, which extends downward from the water table. The water table, although it may fluctuate within several feet each year, is the boundary between these two major zones. Void spaces are filled largely with gases in the unsaturated zone, while the in the zone of saturation they are filled with water.

Commonly, although not in every case, waste liquids must migrate through the unsaturated zone in order to contaminate ground water. The unsaturated zone is exceedingly important because it is here that many chemical and biological reactions occur that attenuate wastes. Unfortunately, undue reliance has been placed on the "living filter" concept of the unsaturated zone, with the erroneous assumption that biological degradation and sorption phenomena will attenuate wastes to such a degree that ground water contamination is not likely to occur. The fallacy of this argument is well substantiated by the thousands of ground-water contamination cases that have been reported. Nonetheless, the unsaturated zone is a major control on ground-water contamination because it exerts a strong influence on the movement of biodegradable and nonconservative substances. Obviously the longer it takes a waste to migrate through the unsaturated zone, the more time and mechanisms there are to attenuate it. In addition to thickness, the major controlling factors are the permeability, grain size, and chemical composition of the earth materials. Generally speaking, those materials that have a high ion-exchange capacity, a low permeability, and consist of fine-grained materials, will have the greatest attenuation effects. Therefore, although not a part of leachate plume mixing and migration in ground water, the thickness and composition of the unsaturated zone must be examined in any waste disposal scheme.

In its simplest form, the movement of ground water can be described by means of Darcy's law, that is, Q = KIA, where Q = the flow rate, K = permeability, I = hydraulic gradient, and A = the cross sectional area through which the flow occurs.

Permeability (K) refers to the interconnection of pore spaces and the ease with which water can move from one point to another. Permeability ranges within wide extremes being greater for coarse materials than for fine.

Permeability is divided into two types: primary and secondary. In the first case the permeability came into being when the strata were deposited, but secondary permeability originated after the rocks became compacted or lithified. Examples of secondary permeability include fractures and solution openings.

The hydraulic gradient is an expression of the slope of the water table and the difference in head or water level is a function of the amount of energy used as the water moves from one point to another. A water-level map is a graphical representation of the hydraulic gradient. Although hydraulic gradient is the driving mechanism for horizontal laminar flow, in certain cases there is a vertical component as well. The vertical component of flow may be either in a downward or upward direction in response to recharge or discharge.

Recharge is the addition of water to a ground-water reservoir. It is derived from the infiltration of precipitation, interaquifer leakage, inflow from streams or lakes, or inadvertently, by leakage from lagoons, leaky sewer lines, etc. Discharge occurs where ground water flows to springs, streams, swamps and lakes, or is removed by evapotranspiration or pumping wells, among others. Pumping wells, by far, has the greatest impact on the hydraulic gradient, locally steepening it several orders of magnitude.

Ground-water velocity is very important in pollution problems, because among other things, it has a major influence on dispersion. The ground-water velocity equation can be derived from Darcy's law and the basic velocity equation of hydraulics. It has the following form: v = KI/n, where n = effective porosity, in percent, and the other terms are as previously defined. Ground-water velocities are generally very small, ranging from a few feet per day to a few feet per year.

The openings in a rock are referred to as its porosity, which is expressed as a percent. Porosity determines the maximum amount of water a rock can contain when it is saturated. Porosity can be divided into the part that will drain under the influence of gravity, which is called specific yield or effective porosity, and the part that is retained as a thin film of water on rock surfaces, which is called specific retention.

Fundamentals of Ground-Water Pollution

In any ground-water pollution study it is essential to obtain the background concentration of a wide variety of chemical constituents, particularly those that might be common both to ground water and a leachate. Since shallow ground-water quality may fluctuate within fairly wide limits during short intervals, it is essential to determine background concentrations by means of several samples taken at different times.

The severity of ground-water pollution is related to the characteristics of the waste or leachate. That is, its volume, composition, concentration of the various constituents, time rate of release of the contaminants, the size of the area from which the contaminants are derived, and the density of the leachate, among others. Data describing these parameters are difficult to obtain.

Once the leachate is formed it begins to slowly migrate through the unsaturated zone where several physical, chemical, and biological forces act upon it. Eventually, however, the leachate may reach saturated strata where it will flow in the direction of the hydraulic gradient. From this point on the leachate will become diluted due to a number of phenomena including filtration, sorption, chemical processes, microbial degradation and dispersion. Dilution will continue but the long-term effects are related to time and distance of travel.

Filtration removes suspended particles from the water mass, including particles of iron and manganese or other precipitates that may have been formed by chemical reaction. Dilution brought about by sorption of chemical compounds, is related largely to clays, metal oxides and hydroxides, and organic matter, all of which function as sorptive material. The amount of sorption depends on the type of pollutant and the physical and chemical properties of the solution and the subsurface material.

Chemical processes are important when precipitation occurs as a result of excess quantities of ions in solution. Chemical processes also include volatilization, as well as radioactive decay. In many situations, particularly in the case of synthetic organic compounds, microbiological degradation effects are not well known. It does appear, however, that a great deal of degradation can occur if the system is not overloaded and appropriate nutrients are available.

Dispersion is a microscopic phenomenon caused by a combination of molecular diffusion, which is important only at very low velocities, and hydrodynamic mixing, which occurs with laminar flow through porous media. In porous media, flow paths have various lengths and leachate transport along a shorter flow path would arrive at an end point sooner than that part following a longer path, thus resulting in hydrodynamic dispersion. Dispersion can be both longitudinal and lateral and the net result is a conic form downstream from a continuous pollution source. The concentration of a leachate is less at the margins of the cone and increases toward the source. Since dispersion is directly related to ground-water velocity, a plume or slug will tend to become larger with more rapid flow.

The rate of advance of a contaminant plume can be retarded if there is a reaction between its components and ground-water constituents or if adsorption occurs. The plume, which tends to have a normal (Gaussian) distribution both longitudinally and transversally, will expand more slowly and the concentration will be lower than those of an equivalent non-reactive leachate. Hydrodynamic dispersion affects all solutes equally, while sorption and chemical reactions can affect various constituents at different rates. Thus, a leachate plume consisting of a number of solutes can have each moving at a different rate due to these attenuation processes.

Monitoring Concerns

Not uncommonly, monitoring wells are placed in a convenient location that may not be the most appropriate from a hydrogeologic perspective. Moreover, little thought may be given to their design and construction. A monitoring system should be designed and constructed to achieve the purposes: (1) determination of hydraulic gradients and (2) evaluation of quality distribution, both in time and space. Since the hydraulic head and ground-water quality may vary vertically, horizontally, and temporaly, the aquifer should be sampled at a considerable number of times, places and depths.

Traditionally monitoring schemes consist of wells of different depths that are distributed throughout the area of concern but which are generally few in number due to cost considerations. One method used to sample the aquifer is to install a single well and slot or screen it at several different depths. In the first case, there may be an insufficient number of wells to adequately describe the vertical and horizontal head distribution, which may be significant in regions of low gradients. In the second case, multiple screened wells provide both composite water levels and water samples, which are useful for determining if a plume exists, but are of limited value for locating the actual position of a plume at depth or its chemical distribution. In recent years it has become a common practice to install a nest of monitoring wells that are closely spaced but of different depths to sample a single interval. The wells may be installed in a single large diameter hole and each gravel packed and grouted at a specific depth.

A number of investigators are beginning to recognize the importance of accurate head and quality measurements and, as a result, a number of innovative monitoring techniques are being developed. A contribution to the wide array of systems is the monitoring well described herein (Fig. 1).

The actual configuration of the monitoring well, particularly slot size and intervals, should be designed to best suit the conditions that have been determined at a pre-drilled site. The well consists of two separate components--an outer slotted casing and a movable packer arrangement that fits tightly within the casing. The materials used to construct the system are dictated by the type of samples to be collected. For example, if the ground water is contaminated by organic compounds, the slotted part of the outer casing should consist of Teflon and that part of the packer assembly that will come in contact with the water sample should be constructed of stainless steel and Teflon. On the other hand, if the contaminants consist largely of inorganic compounds the entire assembly can be constructed from a variety of plastics or metals.

A prototype sampling system consists of 5 cm diameter plastic pipe into the end of which is cemented a cone-shaped plastic plug. Vertical slots (3 mm x 7.6 cm) were milled into the casing. The packer assembly consists of threaded 1 m sections of 12 mm diameter conduit. A grooved circular plate, just slightly smaller than the inside diameter of the casing, is attached to the bottom section. The groove is fitted with a rubber O-ring. Approximately 2.5 cm above the plate is a 6 mm diameter hole in the conduit. A second O-ring fitted plate slips over the conduit; it can be positioned any place on the shaft by means of a set screw. The upper plate is perforated by a 6 mm diameter, 3.8 cm long, brass fitting onto which is attached flexible tubing that is sufficiently long to reach from the bottom of the well to the land surface.

Once the casing is placed in a pre-drilled hole, the upper packer is set at the appropriate interval, for example, .3 m above the base plate, to form a collection chamber. The packer assembly is then slowly forced to the bottom of the well. Water is withdrawn from the well by one of two means. If the water level lies less than about 8 m below land surface, a peristaltic pump may be attached to flexible tubing that is connected to the packer assemblage, which extends above the casing. The water can then be lifted by vacuum directly from the well. If the water level lies at a greater depth, pumping by either air or nitrogen gas is appropriate. The flexible tubing, extending from the upper packer, is attached to the appropriate pressure source, and gas is then slowly allowed to flow into the sampling chamber forcing water through the hole just above the lower packer and then discharging through the center of the pipe. The positive pressure pumping method will allow the collection of a water sample from a considerable depth.

After the first sample is collected, the packer assemblage is pulled up to the next sampling interval and the process is repeated until the entire saturated thickness is sampled. It is important to remove a sufficient volume of water to flush the sampling tube and chamber in order to

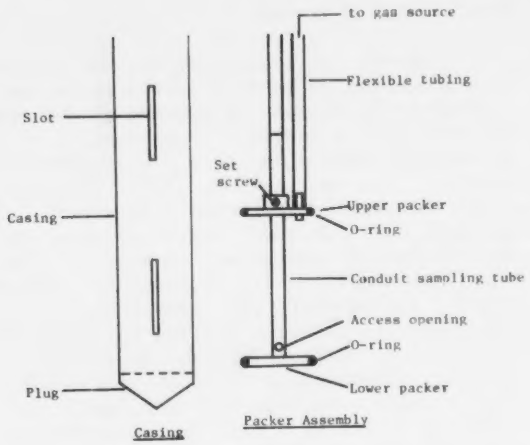


Figure 1. Schematic of monitoring well

collect uncontaminated samples from succeeding intervals. Since the plunger pipe is threaded at regular intervals, sections can be removed as appropriate. Water levels can be measured inside the conduit by means of an electric tape at each sampling interval prior to pumping. When completed the casing should remain in place for subsequent sampling, but the packer assemblage can be used in other wells after it has been thoroughly cleaned.

The monitoring well should be installed in a pre-drilled hole. If the hole is approximately the same diameter as the casing it should be possible to force the casing directly into the hole, which should produce a sufficient seal between the casing and annulus to prohibit vertical leakage along the casing. In some cases fine material may plug the slots and it might be necessary to cement screeens over them, although it might be possible to clear them by injecting gas into the sample chamber, or pumping the well prior to insertion of the packer assembly. Another method is to install this well in a larger diameter hole. In this case the well would be set on the bottom of the hole, gravel poured into the annulus to a position above the top of the bottom sampling interval, and then bentonite or clay would be placed in the annulus, reaching nearly to the next set of sampling slots. The second set of slots are then gravel packed and isolated by another clay or bentonite seal. This is probably the most appropriate procedure and should allow adequate sampling without the need for well development.

Development of Predictive Methods

Introduction

Although seemingly a simple task from a theoretical point of view, the development of ground-water transport models is fraught with uncertainty. Existing models are highly simplified and are not easily adaptable to the complexities of the subsurface environment, changing land use, and density differences between a leachate and ground water, to mention only a few. For example, nearly all ground-water systems include both aquifers and aquitards (confining beds), which can vary widely in thickness and permeability. Differences in permeability between aquifers and aquitards or even between zones of different permeability within a single aquifer, cause refraction of flow lines at their boundaries. As flow lines move from aquifers into and through aquitards, for example, they are refracted toward a direction that is perpendicular to the boundary that produces the shortest path. Consequently, in order to predict the path that a leachate plume will follow, it is essential to determine the location of all units of different permeability since they will cause a change in the flow direction, both vertically and horizontally. This is possible only in the broadest sense.

Models that adequately describe the movement of plumes that are more dense or less dense than water are simply not available. In most cases it is assumed that the leachate density is the same as water density and that there is an even distribution of the waste constituents throughout the thickness of the aquifer. Unfortunately this is not the case where the leachate is less dense due to the presence of light hydrocarbons, such as gasoline, or denser because of highly mineralized solutions.

Another externality that complicates predictive models is the effect brought about by changes in land use. For example, a predicted flow path and velocity may be completely negated if a new well is subsequently turned on, or if an old well is abandoned. In either case there will be a major change in the hydraulic gradient in the vicinity of the well and, therefore, a change in flow path and velocity.

A particularly vexing problem in predicting leachate mixing and migration is the time rate of release of contaminants to ground-water reservoirs. Several investigators have described or illustrated the fact that the chemical quality of water in many shallow and, particularly, surficial aquifers exhibits cyclic fluctuations. These fluctuations are caused by the intermittent flushing of contaminants into the ground during recharge (precipitation) events. The contaminants may be naturally occurring or reflect man's activities, such as waste disposal. The greatest amount of contaminant influx occurs in the spring, but less concentrated and smaller masses may be flushed to the water table at any time. Because of the cyclic nature of recontamination events, care and common sense must be exercised in the extrapolation of quality data, particularly in regard to the prediction of flushing rates and leachate plume mixing and migration.

Several coefficients are required in chemical transport equations and for many of these the data base is inadequate. Examples include reliable field data for dispersion, sorption, and microbiological degradation.

Methods of Development

The philosophy of this investigation is to develop several techniques that can be used to approach the problem of leachate plume mixing that range from broad generalized predictions to much more complicated procedures that require a substantial data base and some expertise in hydrogeology. This approach is based on the premise that some wastes are so innocuous that leachate is not likely to form or be of any significance if it does, and therefore, only a general, pessimistic approach is required. Therefore, only conservative pollutants will be considered. An example is the disposal of demolition wastes, such as fragments of concrete. Some sites are so obviously unsuitable for disposal that only a cursory examination is necessary to bring its inadequacies to focus.

Our predictive scheme is divided into three phases, starting with the most generalized and least quantitative method. The phases are (1) a rating system, (2) analytical-graphical solutions and (3) computer models.

Phase I Rating System

A system for evaluating the contamination potential of waste disposal sites was originally formulated by LeGrand (1964) and has undergone a series of subsequent refinements leading up to a widely used numerical system (LeGrand, 1980). The system focuses on weightening four key geologic and hydrologic characterisitcs in the vicinity of contamination sources. The key parameters are: (1) distance to a water supply, (2) depth to the water table, (3) hydraulic gradient and (4) permeability-sorption, as indicated by the geologic setting. Four digits and four additional letter codes concisely describe the characteristics of a site for standardized interpretation and indicate the relative contamination potential.

Hydrogeologic characteristics at a site are identified on a scale of various aquifer sensitivities to contamination spread, and the particular waste's toxicity, concentration, volume and persistence are identified on a scale of severity of contaminants. These identified positions are integrated into a matrix in which the hazard potential is graphically displayed. The identified position in the matrix reveals the degree of seriousness. The probability of contamination can be determined by correlating a sites numerical description with a synthetic numerical standard in the matrix. Acceptance or rejection standards are suggested that are based first on the natural setting and then on modifications to the site by specific engineering practices.

The system optimizes existing data and provides a useful first round evaluation of all types of leaks, spills and waste disposal sites in relation to nearby ground-water and surface water supplies. An experienced evaluator using the system can assess a potential pollution situation quickly. The system represents a quantification of parameters, appraised graphically in a logical sequence, and the results are indicated in a standardized form that is meaningful to evaluators anywhere. A sample worksheet for the rating system is shown in Table I.

LeGrand's evaluation scheme is useful for the "first-cut" type of waste disposal sites. However, his scheme lacks certain aspects, particularly as it relates to amount and type of expected leachate

TABLE I. RATING SCHEME WORKSHEET

Step 1

Determine the distance on ground between contamination source and water supply

Point value	0	1	2	3	4	5	6	7	8	9
Distance in meters	2000+	1000-2000	300-999	150-299	75-149	50-74	35-49	20-34	15-19	0-14
Distance in feet	6200+	3100-6200	1001-3100	501-1000	251-500	161-250	101-160	61-100	46-60	0-45

Step 2

Estimate the depth to the water table Below base of contamination source more than 5% of the year

Point value	0	1	2	3	4	5	6	7	8	9
Meters	60+	30-60	20-29	12-19	8-11	5-7	3-4	1.5-2.5	.5-1	0
Feet	200+	91-200	61-90	36-60	26-35	16-25	9-15	3-8	0-2	0

Step 3

Estimate water table gradient from contamination site

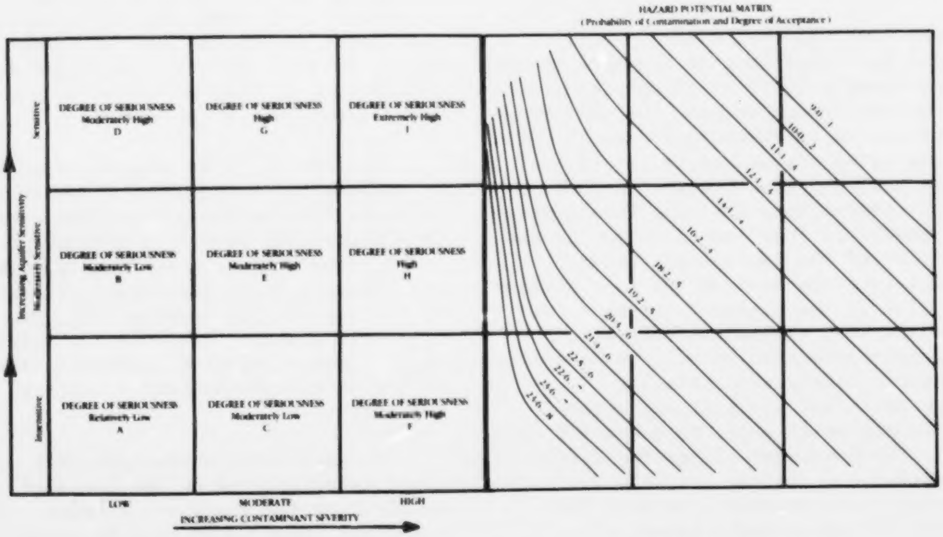
Point value	0	1	2	3	4	5
Water table gradient and flow direction	Gradient away from all water supplies that are closer than 1000 meters	Gradient almost flat	Gradient less than 2 percent toward water supply but not the anticipated direction of flow	Gradient less than 2 percent toward water supply and is the anticipated direction of flow	Gradient greater than 2 percent toward water supply but not the anticipated direction of flow	Gradient greater than 2 percent toward water supply and is the anticipated direction of flow

Step 4

THICKNESS OF UNCONSOLIDATED MATERIALS OVER BEDROCK, IN METERS

	Clay[1]		Clay with no more than 50% sand		Sand with 15-30% clay		Sand with less than 15% clay		Clean fine sand		Clean gravel or course sand		
More than 30	OA[2]		2A		4A		6A		8A		9A		More than 95
	I[3]	II[3]	I	II	I	II	I	II	I	II	I	II	
25-29	0B	1C	1D	2F	3E	4G	5F	6E	7F	8E	9G	9M	75-94
20-24	0C	2C	1E	3D	4D	5E	5G	6F	7G	8F	9H	9N	60-74
15-19	0D	3B	1F	4C	4E	6C	5H	7D	7H	8G	9I	9O	46-59
10-14	0E	4B	2D	5B	4F	6D	5I	7E	7I	9D	9J	9P	28-45
3- 9	1B	6B	2E	7B	5C	7C	5J	8D	7J	9E	9K	9Q	10-27
Less than 3	2B	8B	3C	8C	5D	9B	5K	9C	7K	9F	9L	9R	Less than 10
Bedrock at land surface; I = 5Z, II = 9Z													

THICKNESS IN FEET



Record Description, Par Value, and Rating as noted in example relative to the flow and quality of the naturally occurring ground waters (mixing and resultant plume characteristics). As a first step in developing a more comprehensive set of rules on site selection, we believed that it would be helpful to make additions to LeGrand's scheme to account for the leachate/native ground-water mixing effects. This would be done in such a way to be consistent with the qualitative nature of his scheme and at the same time expand its scope to include additional important pollution considerations. The end result of this first exercise would still be a first cut type of evaluation but with an important expanded scope. A total quantitative evaluation would follow (as described in the next sections of this report) to fully evaluate pollution potential, if need be. A further explanation of this approach is given below and along with an outline as to how it might be incorporated into LeGrand's scheme.

The potential for causing ground-water pollution in the vicinity of a landfill depends not only on the hydrogeologic setting and the characteristics of any landfill contaminant, but also on the quantities of ground water flowing in the receiving aquifer compared with the leachate rate from the landfill. A small amount of contaminant entering a copious aquifer is a much different situation than a large amount of contaminant entering an aquifer of small flow. LeGrand applies this concept in his rating but does not quantify it.

Many landfills and waste disposal scenarios may contribute to leachate having a liquid density quite different than that of the native ground waters. We believe it is important to distinguish between possible leachates being either heavier or lighter than the native ground waters. Pollution potential evaluation, at least in a general sense, should include consideration of the possibility of the contaminant being vertically segregated from the main stream of the flow in the aquifer. Although we are recommending a leachate/aquifer-water density consideration, it must be understood that this is merely a contaminant characteristic not particularly related, pollution potential wise, to something good or bad. The knowledge of density differences earmarks different analysis routes in predicting plume movement, in both the saturated and unsaturated zones.

Finally, a mixing characteristic related to the leachate being either miscible or immiscible in water is needed. Petroleum based liquid wastes are the most commonly occurring immiscible products found in some landfills. The plume characteristics, and pollution potential from immiscible versus miscible liquids, are different for these two distinctive leachate types. If there are immiscible products to be disposed of in a landfill, one should be aware of them for the plume movement analyses.

In summary, we feel that LeGrand's rating scheme needs an additional three descriptors involving (1) the process of dilution of the flowing leachate mixing with the volume rate of flowing native ground waters, (2) the definition of whether the leachate will likely be heavier, the same as or lighter than the native ground waters of the site, and (3) whether any of the leachate liquids are immiscible in water. In each of these cases, the evaluation of pollution potential or the characteristics of the pollution plume movement is different. The procedure for evaluating and characterizing the mixing and the additional plume characteristics follows.

A study is now underway to rank the dilution ratios of the leachate by native ground waters in such a way that will produce numbers between 10 and 1. This would fit LeGrand's general 10 to 1 point system for each of his key hydrogeologic parameters. The dilution ratio would be calculated on the basis of dividing the volume rate of flow of a pollutant by the volume rate of flow of the effective underlying ground-water reservoir.

Another study is underway that is aimed at ranking the seriousness of various concentration levels of pollutant species. This study will result in another 10 to 1 point value number, depending upon whether the drinking water standards are exceeded by factors of, for example, 100, 10, 2, 1, .1, etc., times. (Possibly the point values would involve negative numbers in the case of the native ground waters being of poor quality.)

A final dilution-ranked point value would be calculated on the basis of multiplying the above two numbers. The resultant value would then be added to LeGrand's point system. As a matter of record, a note would be made of whether the leachate is miscible or not and whether it is heavier, about the same, or lighter than the native ground water.

The above procedure is not without some misgivings. First, a sample and quality analysis is needed of the native ground waters. Secondly, some estimate of leachate flow rate must be made (this might be the ground-water recharge rate if no other substantiating data are available). And finally, LeGrand's Hazard Potential Matrices may have to be expanded or readjusted to account for high dilution ratios.

The addition of the dilution and plume density and miscibility characterizations would improve the first-cut evaluation significantly.

Phase II Analytical-Graphical Techniques

One of the basic drawbacks to the LeGrand system is that it is not very quantitative. Many of the point system parameters are given equal weight and others are not. The rationale behind this point system is outlined but the physics of the processes (in terms of laboratory experiments, field determined permeabilities, and widely accepted mass transport equations, for example) are neither documented nor explained. Furthermore, his definitions of such terms as "degree of seriousness, hazard potential, probability of contamination, and degree of acceptance," are opinionated. This is not a criticism of LeGrand's method for what it is as a first-cut evaluation. However, there may be a need for a second-cut evaluation in light of unclear or questionable results of the first cut.

The purpose of developing a more quantitative evaluation method is for clarification purposes. The aim of the quantification process would be to weight the major hydrogeologic parameters in the landfill evaluation process by analyzing known physical and chemical processes that are involved. If we can do this, opinion is minimized until the last step of accepting or rejecting a site. The approach of the quantifying procedure will be as follows.

First, we will study and define a set of widely accepted equations that govern both flow and mass transport of ground water and pollutants from a landfill source. These equations would involve flow and mass transport of pollutants starting from the bottom of the landfill, going downward through any unsaturated zone, and then flowing and mixing horizontally through the unsaturated zone. All of the processes of dilution, dispersion, diffusion, ion exchange, passing of time, radioactive and biological decay would be considered. All of the references contained in this report include such equations of flow and mass transport. There are many other equations also to be considered.

Second, once that the equations are agreed upon, there then exists a mechanism for quantifying the evaluation of a landfill or waste disposal site. Each parameter of the equations can be varied in sequence to illustrate their relative effects on the resulting concentration plume. The weighting system and importance of each parameter can thus be evaluated directly without opinion (other than the assumption upon which the equations were derived). A normalized point system ranging from 1 to 100 would then be devised to display the range of parameter combinations giving the best to the worst case plume concentration distributions.

Third, based upon direct measurement of parameter values or upon lacking data, defining worst case values, solutions of the equations are obtained for the specific site under evaluation. The site specific landfill would then be compared to the above devised point system and a number assigned (or range of numbers depending on the confidence of the input data).

Finally, a judgement (preferably by an EPA official) would be made as to how serious a pollution potential is at the particular site under evaluation based on a single number ranking.

An example of a typical equation that is under consideration for mass transport or plume concentration distribution from a continuous source in a uniform flow is as follows for the saturated zone of flow (see Wilson and Miller, 1978):

$$\frac{f \exp \frac{x}{B}}{4\pi m(D_x D_y)^{\frac{1}{2}}} \cdot W(u,r/B) \tag{1}$$

where

$$B = 2D_x/V \tag{2}$$

$$\gamma = 1+(2B\lambda/V') \tag{3}$$

$$u = r^2/4\gamma D'_x t \tag{4}$$

$$r = \left[(x^2 + \frac{D_x}{D_y} y^2)\gamma\right]^{1/2} \tag{5}$$

$$W(u,\frac{r}{B}) = \int_u^{\infty} \frac{1}{\Theta} \exp - (\Theta + \frac{r^2}{4B^2\Theta})\, d\Theta \tag{6}$$

and

C = solute concentration

f = mass rate of pollutant

D_x,Dy = longitudinal and transverse dispersion coefficients

= $\alpha_x V$, $\alpha_y V$, respectively

n = porosity

R_d = retardation coefficient due to linear, equilibrium absorption

t = time

V = interstial velocity

V' = V/R_d

x,y = coordinates in space with origin at pollutant source and uniform ground-water velocity in x direction

λ = radioactive or biological decay constant

α_x,α_y = longitudinal and transverse dispersivities, respectively

The application of Equations 1 through 6 allows mapping the entire plume concentration distribution eminating from a pollution source as a function of the x and y space coordinates and with respect to time. Despite the apparent complexity of the equation, the solution can be obtained easily with the aid of a pocket calculator. The evaluation of W(u,r/B) is obtained by an algorithm given by Wilson and Miller (1978) in combination with a polynomial approximation of an error function subroutine. An example Radio Shack TRS-80 Basic language program code is given as an example in the Appendix of this report.

Equation 1 allows quantification of the sensitivity of varying dilution dispersive mixing, and degradation parameters. As a simple example, you can observe that if the mass rate of pollutant (f) entering the aquifer is doubled, then the concentration at any point in the downstream plume is also doubled. However, if the aquifer porosity is doubled, the concentration is halved. The other parameter change impacts are less obvious. Consider what happens when the velocity is doubled. Is this necessarily a good situation since there is more water flowing past the landfill with double the velocity? What weight should you give to absorption? The equation is there to answer those questions.

There are many equations available for evaluation of the unsaturated zone also (see Enfield et al., 1980; Warrick, et al., 1971; and Wilson and Gelhar, 1980). It is likely that no more than four equations would be necessary for both the saturated and unsaturated system to quantify the entire flow combinations.

The problem remains as to handling site specific data deficiencies. For example, it is unlikely that dispersivities, hydraulic conductivity, retardation coefficients, porosity, etc., would be available from first- or second-cut type of study. Our quantification scheme would thus involve a study of the literature and a cataloging of case histories of prior pollution studies wherein these unknown parameters were determined and correlated with hydrogeologic evidence of the type that is normally known. Some geologic logs and soil samples are likely to exist and regional hydrogeology is generally known. Estimates could be made of the unknown parameters via the correlation study results. As an example, a description of a geologic log of a test well may be sufficient to estimate hydraulic conductivity (permeability to water). In the event that a satisfactory correlation study cannot reasonably substitute for missing data, then either the permit applicant would be required to initiate a field investigation or a worst case parameter would be chosen for analysis. It is likely that the retardation coefficient will be one of the unknown parameters, in which case the worst situation might be to route the pollutant through the ground-water reservoir without retardation and make a judgement accordingly without observation. An attempt at correlating dispersion, diffusion, porosity, and permeability coefficients with generally known hydrogeologic description is now under study.

Man-made modifications such as bottom liners and compacted top covers can be evaluated by the same set of equations mentioned above.

If possible, the entire quantifying approach will be simplified as much as possible through the use of tables, nomograms, or very simple calculator routines. Presently, this simplification process is uppermost in our work and we will be diligent in keeping it this way as far as possible.

Phase III Computer Models

There will undoubtedly be special cases where neither a first- nor second-cut evaluation of pollution potential from a landfill will yield a satisfactory result for either the permit writer or the landfill owner. Unusual circumstances are likely to occur when the hydrogeologic setting is complicated (stratified, nonhomogeneous, anisotropy, multilayered, or when irregular landfill and external boundary conditions exist, etc.) or when the geochemistry of the pollutant transport is in question (density differences, multiple species involved with numerous possible retardation coefficients, variable leaching rates through unsaturated absorbing type rocks, viscosity and temperature effects, etc.). For these cases, a higher level of evaluation may be in order.

The quantified system for evaluating potential pollution hazards presented in the last section of this report is based upon analytical formulas and basic physical and chemical process consideration. This quantified approach is at a level of sophistication far above an all qualitative approach but lacks a comprehensive capability to account for the above mentioned nonhomogeneities, both in flow and water quality aspects.

There are numerical models available that can account for nonhomogeneities and they may fit into the landfill evaluation process when conditions warrant. Based upon experience, we recommend that numerical models be used with caution since most models are capable of predicting far beyond available data, thus creating a false sense of security. Our approach is to use the simplest model available to solve the evaluation problem.

Several levels of numerical models will be described in the final report. Presently, we are assembling a selection of useable models that can be applied directly or indirectly to the landfill/waste disposal site selection and evaluation process. A review of the EPA report by Bachmat et al., (1978), (which presents a worldwide survey of numerical ground-water models) reveals the fact that less than 16 percent of the flow models and less than 8 percent of the mass transport models reported are useable. Useable was defined as, at a minimum, the existence of an available computer code and a document explaining its application. Based upon our experience, documentation of ground-water computer models is not ordinarily done. There have been numerous models developed and described since 1978 and we are searching the recent literature and contacting several researchers and private firms for more useable codes.

What we want to assemble is a group of numerical ground-water models that can be applied to various aspects of the landfill evaluation process. There is no one numerical model that can solve all of the problems. Particular problems that would be addressed beyond the nonhomogeneities mentioned above are (1) models that could be generated in the vertical as well as the plan view, (2) models that would be applicable to the various geologic environments, such as fractured rocks, karst regions, glacial till areas, alluvial valleys, multiple layered scenarios, etc., (3) models that are simple to operate and can be upgraded as needed to provide detail only to a level appropriate with the problem to be solved--as opposed to super models including many complications beyond which the problem may call for, and (4) models that can handle not only the geochemistry of leachate transport but the related physical density, miscibility, and viscosity problems that are likely to be involved in operating a complex landfill.

The final report on computer models will also contain descriptions of needed computer facilities, the advantages and disadvantages of the selected codes, where help can be obtained in operating and modifying the code for specific applications, and how much time can be expected to be consumed in solving typical problems.

The same point system of the previously described section will be applied to the plume distributions determined from these higher level models. The plume characterizations generated by the higher level computer models are expected to fit within that general evaluation scheme. However, one should expect that the higher level models will be needed for pinpointing and clarifying very specific problems rather than replacing the first- and second-cut type of evaluations.

References

1. Bachmat, Y., B. Andrews, D. Holtz, and S. Sebastian. 1978. Utilization of Numerical Groundwater Models for Water Resource Management. U.S.E.P.A. Publication EPA-600/8-78-012, Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma, 177 pp.

2. Bresler, E. 1973. Simultaneous transport of solutes and water under transient unsaturated flow conditions. Water Resources Research, 9 (4). pp. 975-986.

3. Enfield, C. G., R. F. Carsel, S. Z. Cohen, T. Phan, and D. M. Walters. 1980. Methods of approximating transport of organic pollutants to groundwater. Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma, and Hazard Evaluation Division, Office of Pesticide Programs, Washington, D.C. (in review process.)

4. Hunt, B. 1978. Dispersive sources in uniform ground-water flow. Journal of the Hydraulics Division, Am. Soc. of Civil Eng., Paper Number 13467, HY1. pp. 75-85.

5. LeGrand, H. E. 1964 System for evaluating the contamination potential of some waste sites. Am. Water Works Assn., 56 (8). pp. 959-974.

6. LeGrand, H. E. 1980. A Standardized System for Evaluating Waste-Disposal Sites. National Water Well Association, Worthington, Ohio. 42 pp.

7. Warrick, A.W., J. W. Biggar, and D. R. Nielsen. 1971. Simultaneous solute and water transfer for an unsaturated soil. Water Resources Research, 7(5). pp. 1216-1225.

8. Wilson, J. L., and L. W. Gelhar. 1980. Analysis of longitudinal dispersion in unsaturated flow - Part 1. The analytical method. Water Resources Research. (in review process.)

9. Wilson, J. L., and P. J. Miller. 1978. Two-dimensional plume in uniform groundwater flow. Jour. of the Hydraulics Div. Am. Soc. of Civil Eng., Paper Number 13665, HY4, pp. 503-514.

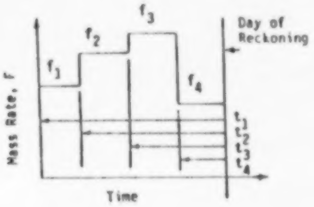
APPENDIX Computer Code For Mapping The Concentration Distribution Of A Plume Of Pollution From A Point Source Of Variable Strength

```
10: "=" : BEEP 3: PRINT "CONTINUOUS POLLUTION"
15: C = 0
20: BEEP 1 : INPUT "UNITS? 1 FOR C--0 FOR G"; H
25: A = 1
30: IF H >0 THEN 50
40: A = 7.48
50: BEEP 1: INPUT "ENTER X VELOCITY ="; V
55: BEEP 1: INPUT "ENTER RETARD. COEF. ="; S
57: Z = V/S
60: BEEP 1: INPUT "ENTER X DISPERSIVITY ="; D
65: B = 2*D
70: BEEP 1: INPUT "ENTER Y DISPERSIVITY ="; E
80: BEEP 1: INPUT "ENTER POROSITY ="; P
85: K = 4*π*P*V*√(D*E)*A
90: BEEP 1: INPUT "ENTER DECAY CONST. ="; L
95: L = LN 2/L/365
97: G = 1 + (2*B*L/Z)
99: BEEP 1: INPUT "ENTER NUMBER OF RATES ="; M
101: FOR W = 1 TO M
103: BEEP 1: PRINT "PREPARE FOR RATE ="; W
105: BEEP 1: INPUT "MASS RATE ="; F
107: A(27+W) = F
109: BEEP 1: INPUT "TIME="; F
111: A(37+W) = F
113: NEXT W
115: BEEP 1: PRINT "RATES DONE--GO AHEAD"
120: BEEP 1: INPUT "OB POINT X ="; X
125: O = EXP (X/B)
130: BEEP 1: INPUT "OB POINT Y ="; Y
140: R = √((X*X + (D/E)*Y*Y)*G)
145: FOR W = 1 TO M
150: U = R^2/(4*G*D*Z*A(37+W))
160: Q = R/B
165: IF (U<1)*(Q<1) PRINT "W(U,R/B) IS INACCURATE"
170: GOSUB 220
180: C = C + ((A(27+W)-A(26+W))*O/K*N
183: BEEP 1: PAUSE "CONCENT. ="; C
185: NEXT W
190: BEEP 2: PRINT "CONCENT. ="; C
200: BEEP 1: PRINT "PRESS ENTER FOR NEW OBPT"
205: C=0
210: GO TO 120
220: J = (Q-2*U)/(2*√U)
222: I = 0
224: IF (J>0) + (J=1) THEN 230
226: I = 1
228: J = -J
229: IF J >55 THEN 245
230: I = I + 1/(1+.0705*J+.0423*J*J+.00927*J^3+.00015*J^4
             +.000277*J^5+.000043*J^6)^16
235: IF I> = 1 THEN 245
240: N = √(π/2/Q)*EXP (-Q)*(2-I)
243: RETURN
245: N = √(π/2/Q)*EXP (-Q)*(I-1)
250: RETURN
```

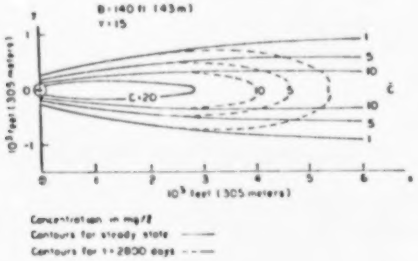
Appendix (Continued)

This program allows entering several sequencial mass flow rates (up to 10) preceeding a chosen day of reckoning for which the concentration distribution plume is desired. The groundwater flow is assumed uniform in the x direction. The effects of dispersion and diffusion, radioactive or biological decay, and ion exchange are allowed. The theory for a constant source is from Wilson and Miller (1978) and should be referred to for details. Superposition holds so that multiple rates and boundary effects may be included if desired.

The variable mas-rate schedule is set up as follows:



A typical output can be mapped as illustrated in the following example (one point at a time with the above program code.)



MECHANISMS AND MODELS FOR PREDICTING THE DESORPTION OF VOLATILE CHEMICALS FROM WASTEWATER

Charles Springer and Louis J. Thibodeaux
College of Engineering, University of Arkansas
Fayetteville, Arkansas 72701

ABSTRACT

Industrial wastewater contains a variety of volatile chemical constituents. The large majority of the volatiles are organics. The general mechanism and kinetics of desorption are well established. Generic flux equations for obtaining emission rates into air from water bodies in the case of flow and non-flow operations are available. What is not generally available are the necessary transport coefficients. Desorption of volatiles can be mechanically influenced or nature driven. Surface aerators, submerged aeration, and thermal evaporation are types of systems that have a dominant mechanical influence. Surface winds, water temperature, and water circulation are important nature driven parameters that regulate rates of desorption in some surface impoundments. The paper presents the available literature information of transport coefficients and establishes conceptual models for those not available. Directions for research on selected transport coefficients are presented. Methods for controlling or reducing desorption from surface impoundments are suggested.

INTRODUCTION

For many years it was generally assumed that all the organic chemicals in industrial wastewaters and processed in biochemical oxidation reactor were either mineralized or converted to biosolids. Little or no thought was given to the fraction that may be volatile and hence transferred to the air phase to result in air pollution. Thibodeaux and Millican (14) developed a test method for determining the fraction of the organic matter that is volatile and reported the volatile fractions for several industrial wastewater. Numerous investigators have detected known volatile chemical species in wastewaters. The fact that volatiles are entering surface impoundments with the wastewater is well established. Air sampling and analysis near surface impoundments and bio-oxidation reactors have detected organics in concentrations above background levels. Several investigations are ongoing to develop methodologies and measure emission rates from these sources (6, 9). In addition, models of a predictive nature are needed.

Verified desorption models provide a means of predicting emission rates from surface impoundments. Field testing is expensive and models can provide an economical alternative. In the case of proposed facilities models provide the only means of assessing the air-pollution impact of treating the wastewater or otherwise impounding the water on the surface for storage, etc.

KINETICS OF DESORPTION FROM WATER

An evaporation process which occurs at temperatures below the boiling point of the liquid involved can be treated by conventional mass transfer rate equations. Typically, the transfer rate is given by Treybal (16).

$$N_A = {}^1K_{A2}(X_A - X_A^*) \qquad (1)$$

where N_A is the molar mass-transfer flux of chemical component A ${}^1K_{A2}$ is the overall mass transfer coefficient based on the gas phase driving force, X_A is the mole fraction in the liquid and X_A^* is the liquid mole fraction of A in the surrounding air.

The coefficient, ${}^1K_{A2}$, can be expressed in the so called "two film" theory or "two resistance" theory as:

$$\frac{1}{{}^1K_{A2}} = \frac{1}{{}^1k_{A2}} = \frac{1}{{}^1H_{XA}{}^2k_{A1}} \qquad (2)$$

Where now ${}^1k_{A2}$ and ${}^2k_{A1}$ are individual transport coefficients for the liquid and gas film respectively. The term H_{XA} is Henry's Law constant in mole fraction form:

$$Y_A^* = H_{XA}X_A \qquad (3)$$

Equation (2) is simply the sum of resistances. If one of the coefficients is very large compared to the other terms, the other resistance is said to be "the controlling resistance". Similarly, the gas phase resistance, $1/H_{XA}{}^2k_{A1}$ can be controlling if the term H_{XA} is very small. Also, if the liquid is a pure material, there is no liquid phase resistance (i.e., water evaporation from a basin), so the gas phase is controlling in such cases. Since H_{XA} for oxygen in water is very large the liquid phase resistance, $1/{}^1k_{A2}$, controls. Often both resistances are important for volatile organics in wastewater.

Desorption rate equation for continuous flow surface impoundments without biochemical oxidation have been developed (15). For a basin in plug flow, the emission rate through the air-water interface is:

$$W_{A0} = W_BX_{A1} \; \{1-\exp(\frac{-{}^1K_{A2}A}{W_B})\} \qquad (4)$$

where W_{A0} is in moles A per time, W_B is the water flow rate in moles per time, and A is the water-air interfacial area. For completely mixed basins the emission rate is:

$$W_{A0} = W_BX_{A1}\{1-1/(1+{}^1K_{A2}A/W_B)\} \qquad (5)$$

Equations (4) and (5) give the maximum emission rates from the basins since X_{A1} is the inlet water concentration. Equation (1) can be used for calculating the flux in subregions of the basin for which X_A is the local surface water concentration. In the case of non-flow basins the emission rate through the air-water interface is:

$$W_{A0} = {}^1K_{A2}AX_{A0} \exp\,(-{}^1K_{A2}At/M_B) \qquad (6)$$

where M_B is the moles of water in the basin, t is time, and X_{A0} is the initial concentration of A in the water. Equation (6) assumes the water is of uniform concentration and no loss of chemical A through biochemical oxidation, absorption on the muds, etc.

Equations (1) through (6) summarizes the kinetics and flux equations for computing emission rates for both flow and non flow basins. The critical parameter for obtaining reliable estimates of emission rates is ${}^1K_{A2}$. This overall transport coefficient is inturn dependent upon ${}^1k_{A2}$ and ${}^2k_{A1}$ as shown by Equation (2). In general good estimates of these two transport coefficients for most wastewater impoundments under all environmental conditions are not available. The following section summarizes the available information on these two transport coefficients for surface water impoundments.

TRANSPORT MODELS AND CONCEPTS FOR SURFACE IMPOUNDMENTS

Table 1 contains a classification of liquid containing surface impoundments. Mechanically influenced impoundments are those that contain some equipment that mixes or adds heat to the liquid. This influence is in addition to that which occurs naturally. Natural processes or nature driven process are the actions of wind, temperature, sunlight, rain, etc. that influence the water environment. The transport coefficients of mechanical influence can be drastically different in magnitude from those of natural processes. These differences must be quantified by appropriate models if realistic flux rate calculations are to be obtained.

Aerated Basins

Aerated Stabilization basins (15) and Activated sludge wastewater treatment basins (3) have received considerable attention with respect to air-stripping of chemicals. The surface of such basins have been divided into two zones. One zone is turbulent (or forced zone) and exists in a region directly influenced by and immediately surrounding each surface aerator. The remain surface is virtually undisturbed by the aerators and is called the natural zone. Two sets of transport coefficients characterize these basins. The total flux rate is the sum of both zones:

$$W_{A0} = {}^1K_{A2}^{(f)}\,(X_A-X_A^*)A_f+{}^2K_{A2}^{(n)}\,(X_A-X_A^*)A_n \qquad (7)$$

where the superscripts denote forced and natural zone coefficients and A_f and A_n are the surface areas of each. The individual

Table 1

Types of Liquid Surface Impoundments

1. Mechanically influenced wastewater impoundments
    - a. Aerated basins-surface and/or diffused aeration
    - b. Thermal evaporation ponds-heat added
    - c. Pan evaporation-heat added
2. Nature driven wastewater impoundments
    - a. Natural evaporation ponds
    - b. Stabilization basins
    - c. Water holding ponds
3. Solvent (non-aqueous) evaporation pits

gas phase coefficient for this zone $^{2}K_{A1}^{(f)}$, is obtained from Reinhardt (10). The individual liquid-phase coefficient for the natural zone, $^{1}K_{A2}^{(n)}$, is obtained from Cohen, etal (2), and the individual gas-phase coefficient for the natural zone, $^{2}K_{A1}^{(n)}$, is obtained from Harbeck (5). $^{1}K_{A2}^{(f)}$ is obtained from the oxygen absorption coefficient (15). The model and respective transport coefficients appear to give reasonable estimates of the methanol emissions from aerated stabilization basins treating pulp and paper industry wastewaters. Table 2 contains a comparison of field measurements and calculated rates (9). A similar methology has been developed for diffused aeration activated sludge system (4). Very low stripping fractions (∿1%) were predicted and verified for acrilonitrile in a high solids activated sludge laboratory scale bio-oxidation reactor. Table 3 contains some typical coefficients.

Pan Evaporation

Hazardous chemical emissions occur to the atmosphere from wastewater produced by the wood preserving industry when "treated" by evaporation methods. The evaporation process can be accelerated by directly applying heat to evaporate the water, as in a thermal pan evaporator. Here the wastewater is piped to an open vessel that uses an external heat source. Merrill, etal, (8) have performed laboratory pan evaporation experiments with pentachlorobenzene and naphthalene in which practically all the chemical dissolved in the water vaporized with the water.

Employing Merrill's data Thibodeaux (13) demonstrated that the emission rate of PCB and naphthalene in high temperature water evaporation is directly related to the water evaporation rate:

$$N_A = N_B(X_A - X_A^*) \qquad (8)$$

where N_B is the water evaporation in moles per area per time. A film theory model for high flux rates was used to support Equation (1). For all pan evaporation experiments combined, N_B = 380 moles/hr·m^2 and $^{1}K_{A2}$ = 360 moles/hr·m^2.

Water Holding Ponds

Holding ponds are often-time used for short or long-term wastewater storage. These ponds are also used as water stabilization basins, natural evaporation basins, run-off catch basins, etc. Holdponds can

Table 2

Aerated Basin Physical, Chemical Data and Methanol Emission (9)

Mill-Visit	H_{XA}	A (Acres)	v_8 (mi/hr)	ρ_{A2} (mg/L)	T (^{o}c)	number observations	meas. flux (ng/cm^2.s)	calc. flux* (ng/cm^2.s)
1-2	.24	127	3.1	23.7	25.0	3	0.10-0.36	.63
1-3	.30	127	6.2	6.0	28.7	6	0.42-4.7	.40
2-1	.29	265	15.8	16.1	28.1	3	2.7 -4.1	2.5
2-2	.38	265	13.2	28.3	33.8	6	.80-4.8	4.9
3-1	.39	7	7.3	14.0	34.4	1	.43	1.6
3-2	.43	7	7.8	-	36.3	4	.069-1.1	1.9
4-1	.43	110	11.8	-	36.2	3	2.4 -3.3	1.7
4-2	.43	110	10.3	9.1	35.6	3	.60-2.8	1.4

*Flux gas phase controlled and Harbeck's correlation used (5).

Table 3

Typical Overall Liquid Phase Volatilization Coefficients

Type of Water Impoundment	${}^1K_{A2}$ (mol/hr·m^2)
Aerated Basins (3)	
Acrylonitrile, calculated, turbulent zone	42500.
Acrylonitrile, calculated, natural zone	210.
Pan Evaporation (13)	
Laboratory test, PCB and Naphthalene	360.
Holding Pond (7)	
Tritium, outdoor basin, field measurements	39.

be generally categorized as open air wastewater vessels in which the chemical desorption forces are nature driven. When wind is present, the correlations for the respective gas phase and liquid phase transport coefficients are the same as in the case of the natural zones of aerated basins and equations developed by Harbeck (5) and Cohen, etal (2) can be used.

It would appear that the emission rate of trace volatile chemicals from aqueous water bodies is drastically reduced in the absence of wind. As noted above, wind is a prime mover of the air and water near the interface and promotes relatively high chemical exchange rates. Even without wind there are still some subtle driving forces which results in a non-zero emission rate. The primary driving forces under a no wind condition appears to be temperature differences across the interface and the direction of water vapor movement.

When the water surface is warmer than the overlying air, an unstable condition is present. The individual gas-phase transport coefficient is affected by air bouyancy which can be quantified by the Grashoff number for heat-transfer. This situation is similar to heat transfer from a hot plate facing upward which has been studied extensively. Using the analogy theories reliable estimates of the gas phase coefficient can be made. The following relation is suggested:

$$Sh_{A1} = 0.14(GrSc_{A1})^{1/3} \tag{9}$$

where $Sh_{A1} \equiv {}^2k_{A1}L/C_1D_{A1}$ is the Sherwood number, $Gr \equiv g\beta_1L^3(T_i-T_1)/\nu^2$ is the Grashoff number for heat transfer and $Sc_{A1} \equiv \nu_1/D_{A1}$ is the Schmidt number.

When the water surface and the air above are at the same temperature but the air is unsaturated there can be water evaporation. Water vapor has a lower molecular weight than the surrounding air so that when evaporation is occuring micro-instability exist immediately above the water surface to promote exchange. Thibodeaux (12) demonstrates how to quantify the individual gas-phase coefficient for this situation based on the Grashoff number for water evaporation. The relation is the same as Equation (9) with Gr replaced by Gr_{B1}, where

$$Gr_{B1} \equiv g\,\zeta_{B1}L^3(Y_{Bi}-Y_B)\nu_1^{\,2} \tag{10}$$

In the case where the air is colder than the water, a stable condition exists and the transport coefficient is likely less than that obtained from Equation (9). When the air is super-saturated with water vapor, there is a net condensation of water at the surface and Equation (10) does not apply. For these stable cases little is known about the nature of the individual gas-phase coefficients and no quantitative expressions have been developed. What can be said is that the process is molecular diffusion controlled and much slower than the unstable case.

All the above was concerned with the individual gas phase transport coefficient. The individual liquid phase transport coefficient also need be quantified if realistic emission rates are desired. If the gas phase transport is not controlling then liquid mixing and renewal of surface layer with water undepleted of the volatile chemical becomes the controlling mechanism. This mechanism is quantified by the magnitude of the individual liquid phase transport coefficient. The direction of heat transfer would appear to also play a significant role in the magnitude of this coefficient.

When the water impoundment is loosing heat through the air-water interface to the surrounding, the water column is unstable since the cooler surface water is more dense than the underlying warm water. The cold water tumbles down just as occurs at lake surfaces during the fall of the year. This plunging cold water is undoubtly effective in bringing chemical species to the surface. No quantitative expressions have been located to obtain estimates of this transport coefficient, however, some oxygen coefficients or heat transfer coefficients for lakes may be available for use as estimates. Since the air layer is also unstable when the water is loosing heat, the combination should give the highest emission rate likely when no wind is present.

When heat is moving from the air to the water, a stable water condition results since warm water tends to float (i.e. thermal stratification). Water mixing is slowed considerbally. Horton, etal (7) report on the rate of loss of tritium from a salt-stratified surface impoundment. Based on their field data, the coefficient shown in Table 3 was obtained. It appears that this emission process is liquid-phase controlled in this case just as it was for pan-evaporation.

Solvent (no-aqueous) Evaporation Pits

Hopefully the storage of pure solvents or solvent mixtures in open pits will be discouraged since evaporation can be extremely high and the associated air pollution and odor problems significant. In the case of pits containing pure solvent or a solvent layer above water, evaporation is gas-phase controlled and highly dependent upon vapor pressure:

$$N_A = {}^2K_{A1}(\rho_A{}^o - \rho_A)/p_T \qquad (11)$$

Where $\rho_A{}^o$ is pure component vapor pressure, ρ_A is the vapor pressure of the volatile species in air and p_T is the total pressure. In the case of mixtures the transport rate may be dependent upon the individual liquid phase coefficient. In general, the emission mechanisms for solvent mixtures will be similar to those from water. Techniques such as those developed by Springer (11), for hydrazene and related compounds, can be used for estimating the emission rates from non-aqueous evaporation pits.

CONTROL OF CHEMICAL DESORPTION

The following is a list of means that can be used to control the emission of volatile chemicals entering surface impoundments:

*maximize biochemical oxidation and minimize desorption through high biosolids and/or pure oxygen,

*build wind fences to decrease the effect of the wind on the transport coefficients,

*cover water surface with a "membrane" (i.e., oil film, ping pong balls, etc.)

*completely enclose the impoundment and scrub or incinerate the exit air, or

*employ alternative treatment or storage which involves no air-water interface.

CONCLUSIONS

*Volatiles can and do escape from surface water impoundments and enter the overlying air mass.

*The general principles and mechanism for the desorption of volatiles from surface impoundments are well established.

*Accurate calculation of emission rates is based on reliable information about transport coefficients in the gas phase and in the water phase.

*Some reliable transport coefficients exist for aerated basins.

*Research is still needed on a variety of surface impoundment transport coefficients, particularly pan or thermal evaporation and the no-wind condition.

*Research is needed in the area of control measures.

REFERENCES

1. Bird, R. B., W. E. Stewart, and E. N. Lightfoot, Transport Phenomena, John Wiley, N.Y., 658-668.

2. Cohen, Y., W. Cocchio, and D. Mackay, Laboratory Study of Liquid-Phase Controlled Volatilization Rates in the Presence of Wind Waves, Environ, Sci, Techno., 12(5):553-558.

3. Freeman, R. A., Stripping of Hazardous Chemicals from Surface Aerated Waste Treatment Basins. In: Proceedings of Air Pol. Control Asso./Water Pol. Cont. Fed. Specialty Conf. on Control of Specific (Toxic) Pollutants, Gainesville, Florida, February 1979.

4. Freeman, R. A., J. M. Schroy, J. R. Klieve, and S. R. Archer, Experimental Studies of the Rate of Air-Stripping of Hazardous Chemicals from Wastewater Treatment Systems, Air Pol. Control Asso. Mtg. Montreal, Canada, June 1980.

5. Harbeck, G. E., A Practical Field Techniques for Measuring Reservoir Evaporation Utilizing Mass-Transfer Theory, Geol. Survey Prof. Paper 272-E, U.S. Govt. Print. Off., Washington, D.C., p. 101-105.

6. Harrison, P. R., R. M. Stockdale, and L. F. Tischler, Development of Sampling and Experimental Methodologies for the Measurement of Hydrocarbon Emissions from Petroleum Refinery Wastewater Systems, U.S. EPA, IREL, Res. Triangle Park, N.C.

7. Horton, J. H., J. C. Corey and R. M. Walace, Tritium Loss from Water Exposed to the Atmosphere,Environ, Sci. Techno., 5(4): 338-343.

8. Merrill, R., Wood Treating Industry Multimedia Emission Inventory, Acurex Corp. Final Report (in preparation), U.S. EPA, IREL, Cinn., Ohio.

9. Parker, D. and L. Thibodeaux, Measurement of Volatile Chemical Emissions from Wastewater Basins, Final report (in preparation), U.S. EPA, IREL, Cinn., Ohio.

10. Reinhardt, J. R. Gas-side Mass-transfer Coefficient and Interfacial Phenomena of Flat-bladed Surface Agitators, Ph.D. Dissertation, University of Arkansas, Fayetteville, Arkansas.

11. Springer, C., Evaporation and Dispersion of Hazardous Materials, Final report, Dept. Air Force, Air Force Office Scientific Research, June 1979.

12. Thibodeaux, L., Chemodynamics - Environmental Movement of Chemicals in Air, Water, and Soil, J. Wiley, New York, 159-162.

13. Thibodeaux, L. and R. Merrill, Pentachlorophenal and Naphthalene Emission to Air During Thermal Evaporation of Wastewater, in preparation.

14. Thibodeaux, L. and J. D. Millican, Quantity and Relative Desorption Rates of the Air-strippable Organics in Industrial Wastewater, Environ. Sci. Techno., 11(9): 879-882.

15. Thibodeaux, L. and D. Parker, Desorption of Selected Industrial Gases and Liquids from Aerated Basins, Amer. Inst. Chem. Eng. Symp. Series 156-Air Pol. and Clean Energy, p. 424-434.

16. Treybal, R., Mass Transfer Operations 3 ed., McGraw Hill, New York, p. 109-111.

MANAGEMENT OF HAZARDOUS WASTE BY UNIQUE ENCAPSULATION PROCESSES

H. R. Lubowitz
Environmental Protection Polymers
13414 Prairie Avenue
Hawthorne, CA. 90250

C. C. Wiles
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

ABSTRACT

The Solid and Hazardous Waste Research Division of the U.S. Environmental Protection Agency has conducted research and evaluation of unique methods for encapsulating hazardous wastes. These methods are intended for the treatment of extremely toxic wastes not readily managed by other treatment processes. Three process schemes have been developed using resins to encapsulate dry unconfined wastes, sludges, and confined or containerized wastes. The processes have been shown to be capable of producing modules of waste that are extremely resistant to physical and chemical stresses.

INTRODUCTION

This paper reviews several studies of unique methods for encapsulation of hazardous wastes. The studies, which were supported by the Solid and Hazardous Waste Research Division, Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency (EPA), grew out of recommendations of earlier hazardous waste studies that had been the basis for EPA's 1974 report to Congress on hazardous waste.[1] These studies had clearly indicated that the hazardous waste problem would require new solutions to accommodate extremely toxic residuals not readily manageable by routine processes. Although available, no detailed descriptions of the encapsulation methods are given here; rather, concepts are presented that offer unique opportunities for processing hazardous materials for long-term, safe retention.

The main objective of the hazardous waste encapsulation program is to develop and/or evaluate unique methods for encapsulating extremely toxic wastes, particularly those that could not be adequately managed in an environmentally acceptable manner by other means. The advantages sought are the following:

- The process should yield high performance products.
- The process should be simple and products are readily reproducible.
- The process without adjustment should be capable of managing wastes with varied compositions and consistencies.
- The process should be versatile (i.e., adaptable to technical advances, changes in wastes, etc.).
- The process should be reasonable in cost (note that a measure of reasonable expense would be relative, depending on the degree of toxicity or hazards associated with the waste and the effectiveness of other available alternatives for managing that waste.).

Ideally, the objective of any hazardous waste management program must be to destroy the hazardous waste completely, to detoxify it, or to recover it for reuse. In reality, however, toxic residues occur that require some type of ultimate disposal. Encapsulation offers an ultimate disposal option in that its objective is to stabilize hazardous material to resist its delocalization by environmental stresses. High performance encapsulation is required in view of the trend to manage concentrated contaminants in order to reduce waste volume in final deposition.

Different ultimate disposal and/or long-term retention options may be considered for encapsulated waste, depending on its final characteristics and the controlling regulatory provisions. If technical considerations alone were used, properly processed encapsulated hazardous material could be stored in salt mines, landfills, or other storage facilities—or they could even be disposed of in the ocean. Placement of encapsulated hazardous waste in a landfill may offer some advantages, such as placement in specifically chosen locations and provision of additional options for controlling the waste (e.g., easy removal of encapsulates if necessary). On the other hand, it may be considered a disadvantage to leave such wastes in place for the concern of future generations. But regardless of which options are used, some form of ultimate disposal is and will probably remain a needed hazardous waste management technique, and the objective of encapsulation must therefore remain as the means to prevent, or at least markedly reduce the rate of, entry of contaminants into the environment.

ENCAPSULATION VERSUS CHEMICAL FIXATION

In proper fixation of a hazardous waste, the contaminants must be dispersed in the molecular and/or colloidal state through the matrix of fixing materials. The chemical affinity of the contaminants and a suitable fixer will stabilize the waste by yielding a composition capable of resisting chemical stresses. Under real conditions, however, this result is difficult to realize because of the many different and changing waste constituents, and the requirement of contaminant solubility. Adjusting the process to specific components in mixed industrial waste gives rise to cost incurring and probably technically difficult tasks.

Perhaps a more realistic goal would be to microencapsulate the contaminant (i.e., to encapsulate each individual particulate of contaminant) by localizing it in a matrix that is chemically stable. The encased contaminants could then exist as particulates in sizes greater than the molecular or colloidal size range and still be adequately stabilized. Whether chemical fixation or microencapsulation, the resulting waste modules must be physically stable and mechanically strong to assure long-term containment of contaminants when placed under stresses expected in manipulation and final disposition. While true chemical fixation appears difficult to achieve, criteria to effect high performance microencapsulation are also exacting, because chemical affinity forces do not come into play to aid the stability of the microencapsulated contaminant in the event flaws or fractures occur in the module. Making insoluble compounds of contaminates (stabilization) prior to microencapsulation must take into account the dispersing effect of aggressive waters as well as its solubilizing effect.

POSSIBLE APPROACHES TO THE PROBLEM

Three general approaches are available to solve the dilemma. These are:

- To tailor the fixation process to the different waste compositions by analyzing the waste and, based on its chemical composition, making appropriate chemical adjustments to the process to handle each of the many different hazardous components or classes of components that might be present. This procedure has proven difficult to accomplish in many cases. (In our opinion, encased contaminant particulates, as well as contaminant fixation, characterized the products of many chemical fixation processes.).

- To employ a generally applicable microencapsulation process rather than chemical fixation, but to assure that each contaminant is sealed within a matrix. This approach is likely to prove difficult because of the exacting processing conditions that are expected to be required to assure that all of the contaminant particulates in a mixed stream are suitably microencapsulated. High performance microencapsulation with minimal amounts of matrix material distinguish such processes.

- To use a generally applicable microencapsulation process and to compensate for probable incomplete contaminant isolation by macroencapsulating the matrix containing the contaminant. Satisfactory macroencapsulation requires use of materials having engineering properties.

The last approach has been the major direction of our hazardous waste encapsulation program, and is judged to offer the best potential for meeting the program objectives. Although we have conducted special evaluations of asphalts and cements, our efforts have concentrated on unique polymeric approaches.

POLYMERIC ENCAPSULATION SCHEMES FOR HAZARDOUS WASTES

Three different waste forms have been considered:

- unconfined dry wastes,
- preconfined (containerized) wastes, and
- sludges

Investigations of methods to encapsulate these waste forms have led to three general schemes: (1) Fusion of resin onto the surface of microencapsulated waste, (2) fusion or spray-on of resin onto preformed casements holding containers of waste, and (3) overpacking of waste containers with welded plastic containers. (See Figure 1 and Table 1.) Physical and mechanical requirements of encapsulates dictate use of macromolecular materials. Organic resins were preferred to inorganic and metallic materials due to greater chemical stability of these materials in the low-in-cost range.

Scheme Description

In scheme I, the polyolefin, high-density polyethylene (HDPE), is fused onto the surface of a polybutadiene microencapsulated waste forming a seamless jacket (macroencapsulation) around the composite matrix. This scheme will accommodate dry (dewatered), unconfined waste, or difficult to dewater sludges made friable by use of a dehydrating agent such as off-specification Portland cement.

Scheme II provides the opportunity to use the fusion techniques of scheme I to encapsulate containers of hazardous waste or to spray-on or brush-on a resin jacket around containers of hazardous materials. The resin jacket is applied to a fiber glass/epoxide substrate encasing leaking and corroding 55-gal drums. The fiber glass encasement is made watertight by fusing or spraying-on or brushing-on the resin jacket. If required, further reinforcement may be obtained by filling voids in the encapsulate with concrete, sand, soil, or other suitable low-cost fillers. HDPE resin fused onto fiber glass casements provided mechanical strength similar to that experienced when resin was fused onto the surface of microencapsulated waste. The sprayed-on resin jacket, however, did not produce similar mechanical properties without repeated applications.

Scheme III involved overpacking of 55-gal waste containers with welded plastic receivers. This scheme resulted from efforts to provide a quick solution for managing corroding and leaking 55-gal drums of hazardous waste. To accomplish this objective, techniques used to weld large plastic pipe were modified and applied to encapsulation. Plastic, 85-gal receivers were used to overpack 55-gal containers of hazardous waste. A seamless container was formed by butt-welding a piece of flat plastic polyethylene (PE) stock to the rotomolded PE 85-gal containers (Figure 2).

Information is available describing studies to produce scheme I, scheme II, and scheme III encapsulates.[2,3,4,5,6,7]

Methods Used in the Resin Fusion Process of Schemes I and II

Three methods can be used for encapsulation by the resin fusion process of schemes I and II (Figure 3): (1) Microencapsulation of waste particulates with polybutadiene and subsequent macroencapsulation of the matrix with HDPE, (2) use of low-cost cementing agents to form a waste

Reproduced from best available copy.

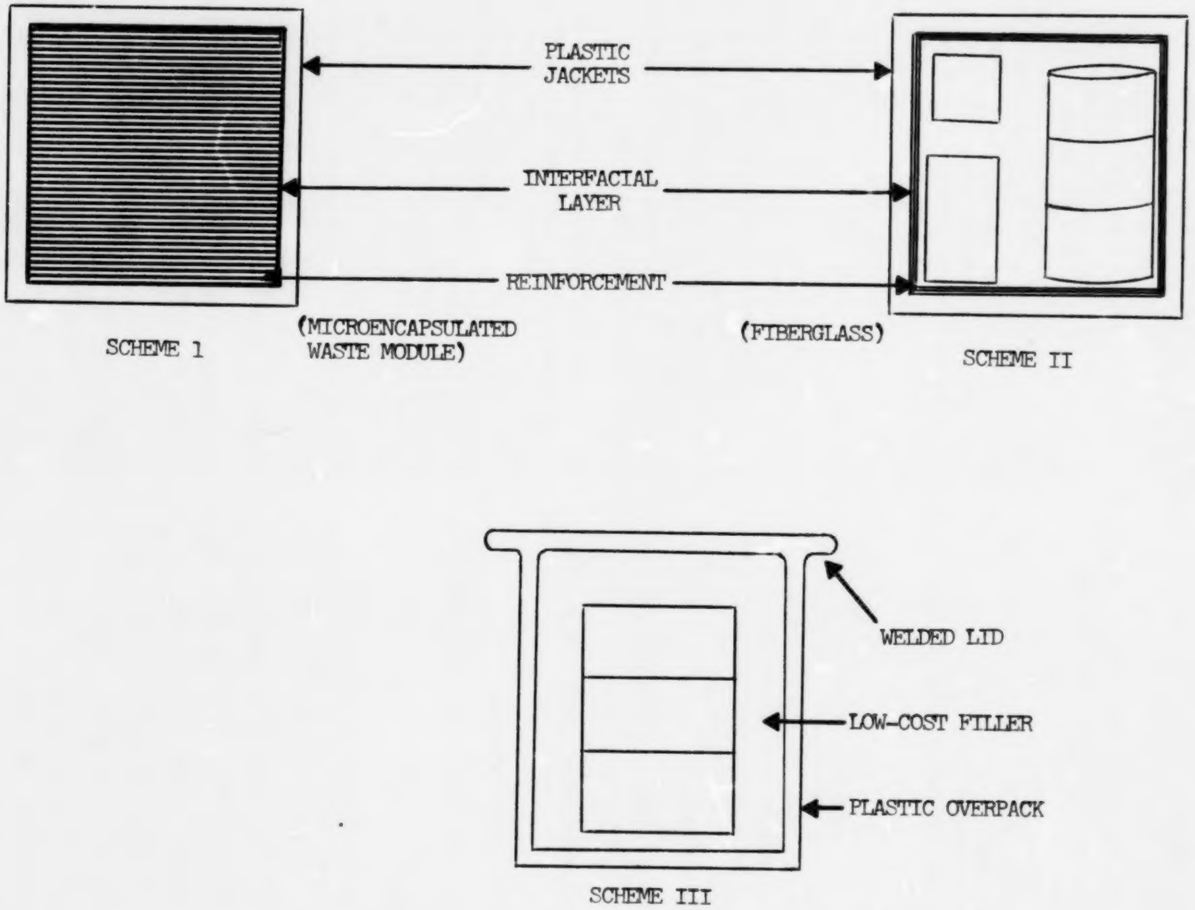

PLASTIC JACKETS
INTERFACIAL LAYER
REINFORCEMENT
SCHEME 1
(MICROENCAPSULATED WASTE MODULE)
(FIBERGLASS)
SCHEME II
WELDED LID
LOW-COST FILLER
PLASTIC OVERPACK
SCHEME III

Figure 1. Three schemes for encapsulating hazardous waste: Scheme I, resin fused onto surface of microencapsulated waste; scheme II, resin fused onto or sprayed onto fiber glass substrate holding containers of waste; scheme III, overpacking of 55-gal waste containers with welded plastic containers.

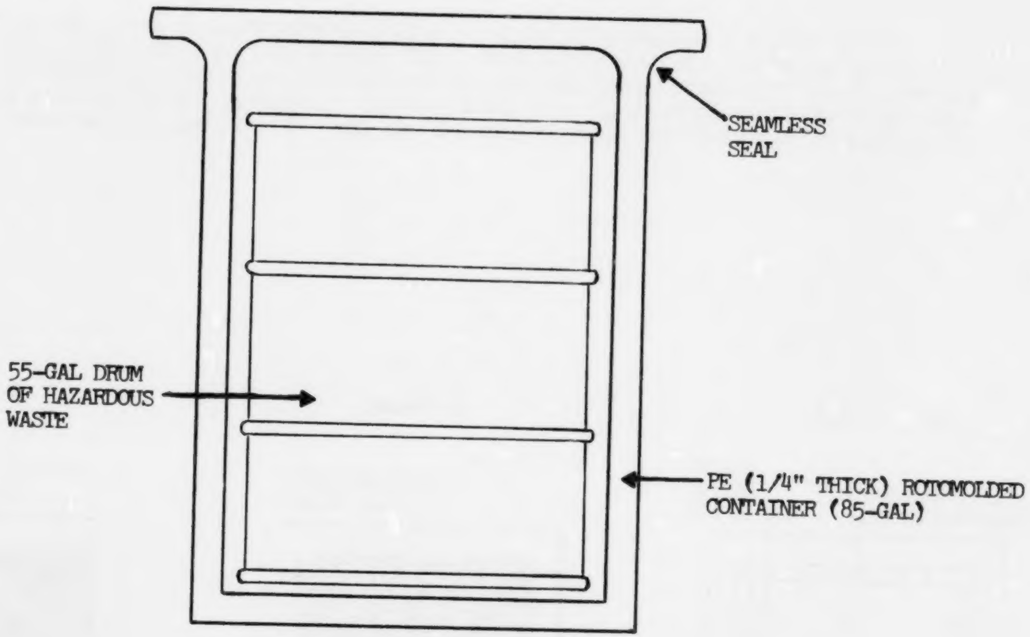

SEAMLESS SEAL
55-GAL DRUM OF HAZARDOUS WASTE
PE (1/4" THICK) ROTOMOLDED CONTAINER (85-GAL)

Figure 2. Plastic overpack system for encapsulating 55-gal drums of hazardous wastes.

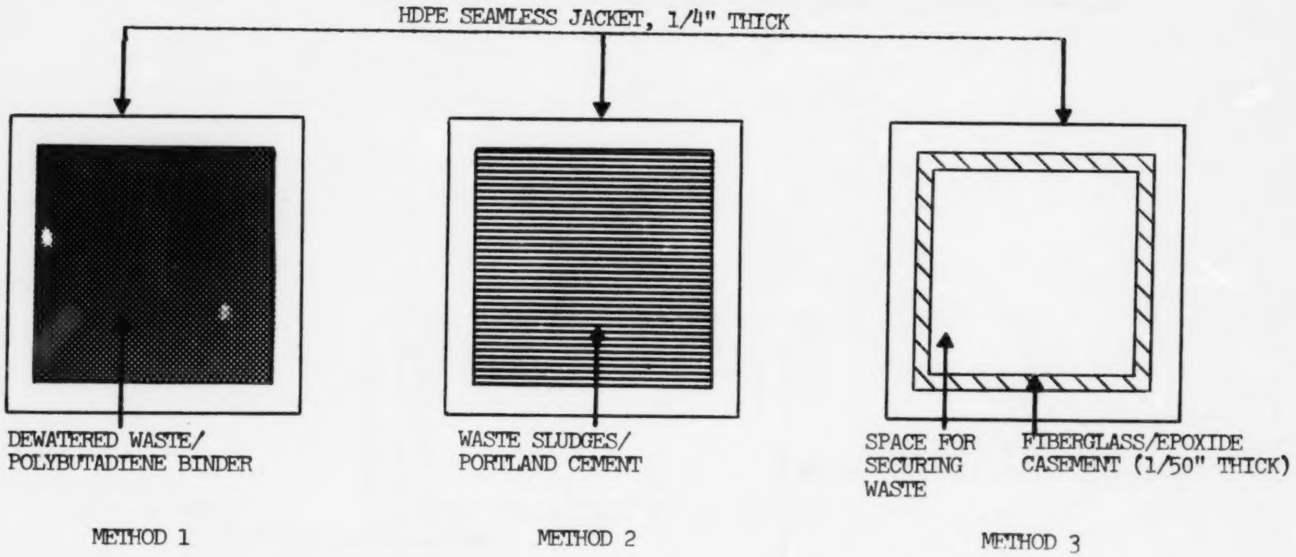

HDPE SEAMLESS JACKET, 1/4" THICK
DEWATERED WASTE/
POLYBUTADIENE BINDER
WASTE SLUDGES/
PORTLAND CEMENT
SPACE FOR
SECURING
WASTE
FIBERGLASS/EPOXIDE
CASEMENT (1/50" THICK)
METHOD 1
METHOD 2
METHOD 3

Figure 3. Three methods that can be used for encapsulation by the resin fusion process of schemes I and II: Method 1, microencapsulation of particulated waste with polybutadiene and subsequent macroencapsulation with HDPE; Method 2, use of low-cost cementing agents to form a waste block onto which the HDPE jacket is fused; Method 3, use of fiber glass/epoxide casement as substrate for HDPE jacket.

TABLE 1. FABRICATION TECHNIQUES AND PREFERRED MATERIALS FOR ENCAPSULATION SCHEMES

Scheme	Waste	Process	Material
I	Unconfined • dry • sludges	Fusion	Polyolefin Polybutadiene
II	Small Containers • 55-gal drums • other	Fusion Spray-on or Brush-on	Polyolefin Glass fiber Glass binder (epoxy or polyester) Concrete
III	55-Gal Drums • other	Welding	Polyolefin

block onto which the HDPE jacket is fused, and (3) use of a preformed fiber glass/thermosetting resin casement as a substrate for the HDPE jacket.

In the first method, 1,2-polybutadiene is mixed with the particulated waste which, after solvent evaporation, yields free flowing dry resin coated particulates. Further processing involves the formation of a block of the polybutadiene/waste mixture by the application of moderate heat and pressures in a mold. The final encapsulated module is produced by fusing a 1/4-inch-thick HDPE jacket onto the block.

The second method involves the use of low-cost cementing agents such as Portland cement to form the waste block onto which the HDPE jacket is fused. This modification provides the opportunity to process sludges without having to form particulates and the limited number of wastes that are not compatible or will not agglomerate with polybutadiene.

The third method employs a fiber glass thermosetting resin matrix as a substrate for the HDPE jacket. Powdered HDPE is fused onto fiber glass which yields receivers to contain hazardous waste, which is usually containerized. The receivers are then sealed with additional fiber glass (for the lid) and the HDPE.

POLYMER SELECTIONS

The selection of polymers for forming the encapsulated modules was based on factors consistent with the program objective—to provide a cost effective system capable of managing extremely hazardous waste. A rather intensive screening of available polymers resulted in the conclusion that the polyolefins, and particularly PE, offered the best overall advantages. PE is mass produced, well characterized, relatively low in cost, excellent in chemical stability, and flexible with mechanical toughness. The use of PE for macroencapsulation is common to all three resin fusion methods discussed and to the pipe-welding scheme.

Polymers Selected For Method 1 of Scheme I

Microencapsulated Matrix/Macroencapsulated Module

To form the microencapsulated waste block (the block onto which the macroencapsulate is formed by resin fusion), a thermoset resin was produced from 1,2-polybutadiene and powdered PE resins. Crude polybutadiene and scrap PE are acceptable as well as virgin materials. The polybutadiene was thermoset by peroxides, as employed in peroxide vulcanization of rubber. By contrast, however, the 1,2-configuration gives a high yield of chemical cross-links in a fast chemical reaction. The resulting polymers have singly bonded carbon backbones, which provide resistance to oxidative and hydrolytic degradations and to permeation by water. Furthermore the polybutadiene possessed characteristics that aided processing and provided desirable chemical and mechanical properties. The resin-treated waste particulates were free-flowing and stable under atmospheric conditions, provided they were sheltered from the sunlight. This is an advantage

Reproduced from best available copy.

not available with two-component resin systems where reaction proceeds upon combination of the two parts. This stability permitted the subsequent microencapsulation step to be scheduled as time permitted. In addition, the chemical nature of the 1,2-polybutadiene and the thermosetting reaction assures reproducible encapsulation of waste particulates, even when their chemical compositions and consistencies are mixed. In the subsequent fusion step, powdered high-density PE grafted chemically onto the polymer backbones and provided the final matrix with ductile qualities. Various combinations of the two resins (i.e., 1,2-polybutadiene and PF) permitted tailoring of the matrix mechanical properties without reduction of system stability when exposed to severe chemical stress.

The macroencapsulated module is seam free, and observations showed the 1/4-inch-thick HDPE jacket to be mechanically and chemically locked to the surface of the block of microencapsulated waste. If desired, variations in processing conditions will permit controlling the degree to which the PE bond penetrates the surface of the agglomerate, providing additional mechanical and chemical resistance. This control is an outstanding feature of the resin fusion process. It also makes low tolerance machined, simple molds suitable for fusing resin jackets onto microencapsulated waste.

Polymers Selected for Method 3 of Scheme II

In the case of the spray or brush-on system of scheme II, recent developments with aliphatic polyurethanes suggested that a formulation using a water-based polyurethane could be developed that would yield tough, flexible coatings upon atmospheric curing. As a class atmospheric curing resins normally yield brittle coatings. Additional studies produced a formulation and a process that permitted the brushing or spraying on of a tough, flexible coating to a preformed fiber glass epoxide casing (method 3). Excellent adhesion of the polyurethane overcoat to the glass casing was attributed to hydroxyl groups stemming from the epoxide and interacting with the polyurethane in curing. For field operations, the use of water based polyurethane has advantage over organic solvent entrained polyurethane. Although the encapsulates were watertight, the major problem with the system was that it required the application of more than one coat to provide the stringent mechanical properties desired for manipulating the ensemble. We are confident that additional materials research would yield ways to overcome this problem. At the present stage of development, spray-up method can be used to stop or prevent leaking of hazardous materials from malfunctioning containers.

Polymers Selected for Scheme III

For the 55-gal drum overpack system of scheme III, rotomolded wide-mouth, medium-density PE receivers, normally used as liners for vessels, were selected. Flat stock of high-density PE was selected for welding a lid onto the wide-mouth receiver. These items were commercially available and required only slight modifications to accommodate our objectives. The welding apparatus, frame, and auxiliary equipment were either adapted from the plastic pipe welding industry or fabricated to meet our specific needs.

The use of dissimilar materials to encapsulate 55-gal drums demonstrated that materials need not be matched for making proper closures. The materials employed were those most readily available. In a scale-up operation, materials and closure design would be specified to facilitate product fabrication and assure quality control.

PERFORMANCE EVALUATIONS

Specimens of encapsulated modules have been subjected to various chemical and mechanical stresses. Tests were designed to evaluate the modules' resistance and capability for isolating the encapsulated contaminants from the environment.

Resin Fusion Methods (Schemes I and II)

In laboratory tests of leaching resistance, modules containing extremely difficult to manage hazardous wastes were encapsulated by each of the three resin fusion methods (Table 2) and exposed to rather harsh environments for up to 120 days. Solutions to which these modules were exposed included, for example, 1.5N HCl, NaOH, citric acid, $(NH_4)_2S$, Dioxane, NH_4OH, etc. Results indicated excellent retention of contaminants, including difficult to contain arsenic-bearing salts and hazardous sodium salts.

TABLE 2. WASTES MANAGED IN TESTS OF RESIN FUSION METHODS

Method	Waste
1	Dewatered sludges:
	Electroplating
	Battery
	SO_x scrubber
	Pigment
	Chlorine, calcium fluoride
	MSMA (monosodium methanearsonate)
2	As_2O_3 (copper smelters)
	As_2S_3
3	Aqueous solutions of salts
	Cu, Cr, Ni, Cd, Zn, Pb, Sb,
	As, Hg, Se

In tests conducted at the U.S. Army Corps of Engineers Waterways Experiment Station, the resin fusion process successfully managed the wastes indicated in Table 3. These tests involved exposure of encapsulated modules placed in columns and exposed to leaching solutions over a 2-year period.[8,9]

Specimens of encapsulated modules were also evaluated for resistance to mechanical and physical stresses, (i.e., compression, freeze-thaw, impact strength, puncturability, bulk density, drop test, etc.). Results showed that the encapsulated modules can be expected to withstand mechanical and physical stresses greater than those expected during handling, transportation, and disposal/storage. Details of the chemical and mechanical tests are available.[2,3,8,9]

Overpack Method (Scheme III)

The modules resulting from scheme III, which involved waste containers overpacked with welded plastic containers, did not provide the structural stability of schemes I and II, even though they were seamless. This is as expected because the plastic jackets were not reinforced as in schemes I and II (see Figure 1). Additional structural stability may be obtained by filling the empty spaces between the overpack and the inner container with cement or foamed resin. Chemical stability was not tested but is expected to be similar.

COSTS

Some preliminary costs have been estimated for the encapsulation processes discussed in Table 4. Commercial resin costs were determined to account for more than 50 percent of the production costs for the resin fusion option. The use of scrap materials should help to reduce these costs significantly.

Cost can be a relative matter. For example, the fact that these processes may be the only existing techniques that can effectively manage certain hazardous wastes must be factored in with other cost considerations.

Other cost evaluations have indicated that encapsulation techniques have relatively low life-cycle costs, indicating that overall costs are favorable when compared with other processes.[10] But detailed cost estimates for these processes cannot be accurately developed without additional pilot scale and field work.

TABLE 3. ENCAPSULATED WASTE EVALUATED AT THE U.S. ARMY WATERWAYS EXPERIMENT STATION

Code No.	Source of Waste	Major Contaminants
100	SO_x scrubber sludge, lime process, eastern coal	Ca, $SO_4^{=}/SO_3^{=}$
200	Electroplating sludge	Cu, Cr, Zn
300	Nickel - cadmium battery production sludge	Ni, Cd
400	SO_x scrubber sludge, limestone process eastern coal	Cu, $SO_4^{=}/SO_3^{=}$
500	SO_x scrubber sludge, double alkali process eastern coal	Na, Ca, $SO_4^{=}/SO_3^{=}$
600	SO_x scrubber sludge, limestone process, western coal	Ca, $SO_4^{=}/SO_3^{=}$
700	Pigment production sludge	Cr, Fe, CN
800	Chlorine production brine sludge	Na, Cl^-, Hg
900	Calcium fluoride sludge	Ca, F^-
1000	SO_x scrubber sludge, double alkali process, western coal	Cu, Na, $SO_4^{=}/SO_3^{=}$

TABLE 4. ESTIMATED COSTS OF ENCAPSULATION

Process Option	Estimated Cost
Resin Fusion:	
Unconfined waste	$110/dry ton
55-Gallon drums	$0.45/gal
Resin spray-on	Not determined
Plastic Welding	$253/ton = $63.40/drum (80,000 55-gal drums/year)

Unique Properties and Advantages of the Polymer Encapsulation Techniques

The polymeric encapsulation schemes are considered unique. These systems offer exceptionally high resistance to rather severe chemical and mechanical stresses. Unlike other polymeric systems, the resin fusion process does not require the mixing of 2 components, thus not constraining the process to timed operations. This feature provides flexibility in processing. In addition, the 1,2-polybutadiene/PE system has characteristics that permit unusually high loading of the filler (waste). The final encapsulated product can contain approximately 94 percent waste by weight. This percentage may vary some from waste to waste. But such high loading capacities make this polymer system unique when compared with most others, and they provide economic advantages with regard to processing and materials.

Another advantage of the polymeric systems is that they can accept a wide range of waste types without modifications. The processes can, however, be rather easily tailored for specific circumstances. Although laboratory and pilot processing steps and equipment used may appear somewhat complicated and/or sophisticated, they are not. Full-scale systems and processes are expected to be rather simple to conduct.

SUMMARY AND CONCLUSIONS

This paper discusses concepts for using polymers to encapsulate hazardous wastes. Polyolefin (primarily high- and medium-density polyethylene), polybutadiene, polyurethane, and fiber glass/epoxides have been used to produce encapsulated modules of hazardous waste. Modifications of these polymer systems have made it possible to produce encapsulated modules capable of handling different waste forms—dry unconfined wastes, sludges, and containerized wastes. The encapsulation systems are compatible with a wide range of waste compositions, and the modules they produce have been shown to have high resistance to chemical and mechanical stresses. They can be expected to provide hazardous waste containment over exceptionally long periods of time. The nature of the systems is such that they can be tailored to different waste characteristics and containment objectives. For example, the encapsulated waste can be stored under strict control and removed if required, or it can be disposed of under various regimes.

Details of the processes discussed in this paper are available as noted in the references. Each process discussed is in a different stage of development. The polybutadiene/PE resin fusion system for dry unconfined waste is completed at the laboratory stage and a full-scale engineering process and equipment design has been set forth. The spray-on system requires additional material R&D to produce structurally acceptable coatings in one application. The plastic weld overpack system is essentially under full-scale development because of its nature. Only limited specimens, however, have been produced. Some additional pilot-scale work is required, followed by a field demonstration of techniques.

Though uncertain, the preliminary economics of these systems appear to be acceptable. If future cost considerations take performance capabilities into account, these systems are expected to become more economically viable.

REFERENCES

1. "Disposal of Hazardous Wastes," Report to Congress, SW-115. U.S. Environmental Protection Agency, 1974.

2. Lubowitz, H. R., et al. Development of a Polymeric Cementing and Encapsulating Process for Managing Hazardous Wastes. EPA 600/2-77-045, U.S. Environmental Protection Agency, Cincinnati, Ohio. 1977.

3. Lubowitz, H.R., and C. C. Wiles. Encapsulation Technique for Control of Hazardous Wastes. In: Toxic and Hazardous Waste Disposal, Volume I, R. B. Pojasek, ed. Ann Arbor Science, Ann Arbor, Michigan, 1979. pp. 189-232.

4. Lubowitz, H. R., et al. Encapsulation of 55-gal Drums Holding Hazardous Wastes. In: Proceedings of the Sixth Annual Research Symposium—Treatment of Hazardous Waste, March 1980. EPA 600/9-80-011, p. 43.

5. Lubowitz, H. R. , and R. W. Telles. Study of Encapsulate Formation with Polyethylene Resin and Fiber Glass for Use in Stabilizing Containerized Hazardous Waste. Draft Final Report, Contract 68-03-2483, U.S. Environmental Protection Agency, Cincinnati, Ohio. 1980.

6. Lubowitz, H. R., et al. Encapsulation of 55-gal Drums of Hazardous Waste by Welding Polyethylene Resin. Draft Final Report, Contract 68-03-2483. U.S. Environmental Protection Agency, Cincinnati, Ohio. 1980.

7. Lubowitz, H. R., and R. W. Telles. Encapsulating Hazardous Waste by Spraying or Brushing On Atmospheric Curing Resins. Draft Final Report, Contract 68-03-2483. U.S. Environmental Protection Agency, Cincinnati, Ohio. 1980.

8. Mahloch, J. L., D. E. Averett, and M. J. Bartos, Jr. Pollutant Potential of Raw and Chemically Fixed Hazardous Industrial Wastes and Five Gas Desulfurization Sludges—Interim report. EPA 600/2-76-182, U.S. Environmental Protedtion Agency, Cincinnati, Ohio. 1976. 105 pp.

9. Bartos, J. J., Jr., and M. R. Palermo. Physical and Engineering Properties of Hazardous Industrial Wastes and Sludges. EPA 600/2-77-139, U.S. Environmental Protection Agency, Cincinnati, Ohio. 1977. 77 pp.

10. Hansen, W. G., and H. L. Rishel. Cost Effectiveness of Treatmeet and Disposal Alternatives for Hazardous Waste, Volume I. Draft Final Report, Contract 68-03-2754, U.S. Environmental Protection Agency. 1980.

ESTIMATION OF POLLUTION POTENTIAL OF INDUSTRIAL WASTE FROM SMALL-SCALE-COLUMN LEACHING STUDIES

Philip G. Malone
Larry W. Jones
Richard A. Shafer
Robert J. Larson

Environmental Engineering Division
U. S. Army Engineer Waterways Experiment Station
Vicksburg, MS 39180

ABSTRACT

Two industrial wastes, a nickel-cadmium battery sludge and a pigment production sludge, and three solidified/stabilized products produced from them were subjected to long-term leaching in small (10 cm diameter by 122 cm) plexiglas columns. Leachate from untreated nickel-cadmium battery sludge contained large amounts of soluble salt (probably mostly sodium nitrate) and exceeded drinking water standards for mercury, manganese and selenium. The pigment production sludge produced leachates exceeding drinking water standards for cadmium, chromium, mercury, manganese, lead, and sulfate. Of the three solidification/stabilization processes evaluated, the process using soluble silicate and cement additives gave the best containment of the heavy metals, but exceeded the untreated sludges in initial losses of soluble species. A flyash and lime additive process produced a product which lowered the overall conductivity of the leachate but did not significantly lower the losses of the heavy metals. A urea-formaldehyde treatment process greatly increased the rate of loss of most contaminants to the leachate. The overall effect of the treatment processes on contaminant loss may be lessened because of the relatively low loss of pollutants from the untreated sludges. After 2 years leaching time, much less than 1 percent of all heavy metal pollutants had been leached from any of the sludge samples except from the urea-formaldehyde treated sludge.

INTRODUCTION

The investigation reported here assesses the pollutant potential of two industrial wastes. Parts of this work have previously been reported (1,2,3). Also addressed is the effectiveness of three sludge solidification/stabilization processes in preventing the loss of constituents from treated and untreated sludge specimens under controlled long-term, submerged conditions. Two of the three processes are currently being used to treat selected industrial wastes on a commercial basis; the third (the urea-formaldehyde resin) has been used extensively in handling and transport of radioactive waste for several years and has been suggested for industrial waste applications (1).

Two common, waste sludges which have high concentrations of toxic heavy metals are included in this study -- a nickel-cadmium (Ni-Cad) battery sludge and a pigment production sludge. Ni-Cad battery sludges are produced during the precipitation of nickel and cadmium from their nitrate salts to form the battery electrodes. The metals precipitate as the solution pH is increased to 11 or 12 by the addition of sodium hydroxide. The excess hydroxides and any other materials remaining in the suspension of spent salts are settled out to form the sludge. This sludge typically has a high slurry pH (12 to 12.5), low solids content (35 to 45 percent solids), and contains greater than 1.0 percent dry weight of calcium, nickel, chloride, and silicon (Table 1).

TABLE 1. SELECTED PHYSICAL PROPERTIES AND LEACHING COLUMN LOADING OF TREATED AND UNTREATED SLUDGES

Parameter	Ni-Cad Battery Sludge (#300)			Pigment Prod. Sludge (#700)	
	Untreated	Process A	Process B	Untreated	Process C
Physical Properties:					
% dry sludge solids	45	21	40	41	26
Slurry pH	12.3	12.7	9.8	8.4	4.8
Specific gravity	3.96	2.71	3.68	3.09	1.74
Median grain size (mm)	0.044	(solid)	0.125	0.016	(solid)
Permeability (10^{-6} cm/sec)	5.70	1.91	1.89	6.51	160
Leaching Column Loading:					
Final product in column (Kg)	13.8	8.5	8.1	11.7	5.6
Dry sludge solids in column (Kg)	6.15	1.78	3.26	4.83	1.14

Other ions usually present at greater than 1 g/kg dry solids are cadmium, iron, magnesium, and zinc.

The paint pigment sludge is produced by treating waste water with lime, sodium sulfide to precipitate the metals, and an organic polymer to aid settling. Ferris sulfate is then added to remove the excess sulfides. This sludge is typically weakly alkaline (pH 8 to 9), has low solid content (25 to 35 percent solids), and has greater than 1.0 percent dry weight of calcium, chromium, iron, magnesium, lead, chloride, sulfate, and silicon. Other metal ions present at greater than 1 g/kg dry solids in the sludges used in this study are cadmium, copper, magnesium, nickel, and zinc. Both sludges present a high probability of environmental pollution if disposed of by shallow land burial.

In the leaching method used, treated and untreated sludges are placed in small (10 cm diameter) plexiglass leaching columns. Water saturated with carbon dioxide was flowed around or through the sludge for periods of up to 2 years. The leachate produced was collected at progressively increasing time intervals and analyzed for selected constituents. The results of these analyses were used to evaluate the pollutant potential of the two industrial waste sludges and the effectiveness of the treatment processes to contain the sludge constituents.

METHODS AND MATERIALS

Solidification/Stabilization Procedures

Sludges used in this study were mixed thoroughly and divided into several subsamples. A subsample of the two sludges were sent to three processors for preliminary evaluation and testing. Two of the processors (A and B) declined to treat the pigment production sludge but did submit samples of treated Ni-Cad battery sludge for leach testing. The third processor (C) declined to treat the Ni-Cad battery sludge but did submit treated samples of the pigment production sludge for leach testing. In each case, the effectiveness of the treatment process is evaluated on the basis of leaching columns containing untreated samples of the same sludge type.

The solidification/stabilization processes used in this study are proprietary. Therefore details on the exact composition of additives and the exact proportions used are not available. The general nature of each process, however, has been supplied by the processors (2). The processors are identified here by letter only and no further information can be supplied.

Process A--

This patented process uses bituminous flyash and a "lime additive" to produce a pozzolan product with good structural integrity. The amount of bituminous flyash added is related to the amount of total solids in the waste being treated. The sludge remains alkaline during the entire process. The sludge was dewatered by settling. Approximately 50 kg of the solidified product was prepared and cast into 7.6 cm x 40 cm cylinders using standard concrete-testing molds. The molds were cured for 30 days under humid conditions to prevent cracking. Specific additive to sludge ratios were not provided by the processor, but the percent of dry sludge solids in the final product was 21 percent. A solidified sample of the product is shown in Figure 1.

Process B--

This process which is also patented, uses a soluble silicate and a cement based additive to produce a "soil-like" material. The consistency of the final product can be varied to suit the product characteristics required, but for landfill disposal, the "soil-like" material is the most economical to produce. Molds 120 cm^2 x 9 cm deep were covered with polyethylene during the 12-day curing period. The cured specimens were broken into irregular chunks, 2 to 5 cm in dimension and placed in leaching columns without compaction. The final product contained 40 percent dry sludge solids. Figure 1 shows samples of the final product which were broken to fit into the leaching column.

Process C--

This process uses a patented urea-formaldehyde resin formulation (with sodium bisulfate catalyst) to produce a solid, rubber-like material. The polymerization reaction requires an acid medium which is provided by the addition of sufficient sodium bisulfate solution to provide a pH below about three. The sludge-resin mixture polymerizes rapidly in the 7.6 x 40 cm molds. Since the reaction is rapid, no curing period is necessary. Any weep water produced was allowed to evaporate on the surface of the mold. The final product contained 20 percent dry sludge solids and is shown along with the untreated, pigment production sludge in Figure 2.

Column Leaching Procedure--Between 8 and 12 kg of each of the treated and untreated sludges were loaded into three identical leaching columns (see Table 1). Leachates from one column of each set of three was randomly selected for analysis with very sensitive techniques (high precision columns); samples from the remaining leaching columns were analyzed using conventional, flame-atomic-absorption methods (low precision columns). Statistical analyses were only carried out where parameters of the leachate from all three columns were above the higher detection limits. Analyses from the high precision columns alone are used for those constituents present below the detection limits of the higher precision techniques. Detection limits of the two analytical methods are presented in Table 2.

The leaching columns were made from 1.5 m lengths of 10.16 cm ID plexiglass pipe as shown in Figure 3. The bottom of each column was closed with a perforated plate that allowed the leachate to drain into a 1.27 cm deep collecting well. The leaching fluid was introduced through a tube entering the column 19 cm from the top of the column. The tops of the column were covered with loose-fitting plastic lids to prevent dust from entering. The flow of leachate water through each column was regulated with a Teflon stop-cock. A 7.5 cm layer of polypropylene beads (60 mm diameter) was packed in the column to retard the movement of particulate material into the collecting well. Leachate from each column was collected in a 4.5-ℓ polyethylene bottle located below the column. A view of the columns taken during the leaching experiment is shown in Figure 4.

Untreated sludges were placed directly in the columns and back-flooded with distilled water to remove all air bubbles. The fixed sludge samples that were not cast into cylinders were broken

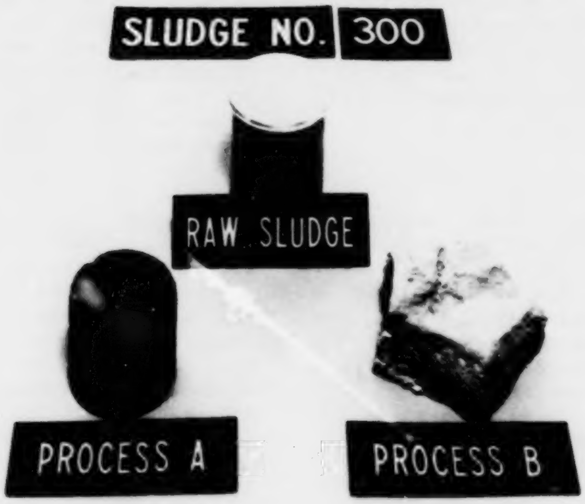

SLUDGE NO. 300
RAW SLUDGE
PROCESS A
PROCESS B

Figure 1. Samples of treated and untreated Nickel-Cadmium battery sludge

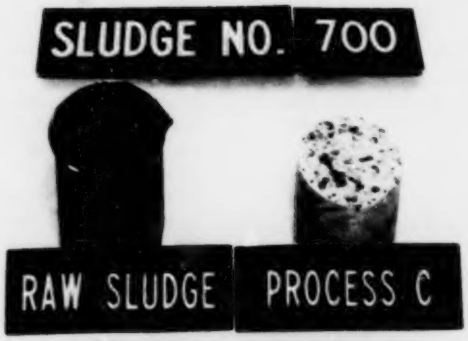

SLUDGE NO. 700
RAW SLUDGE
PROCESS C

Figure 2. Sample of treated and untreated pigment production sludge

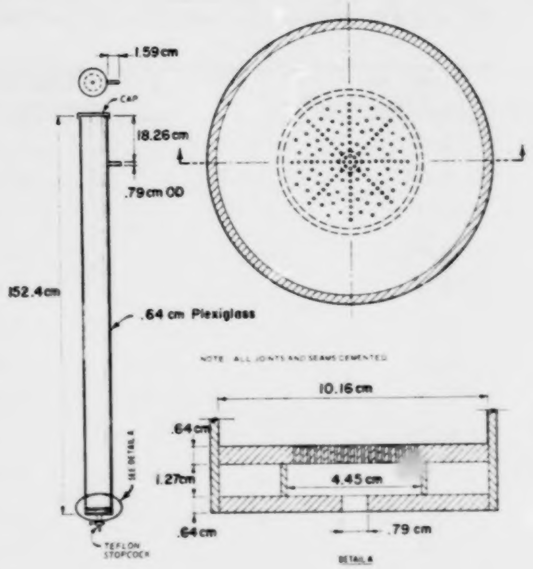

1.59cm
CAP
18.26cm
.79cm OD
152.4cm
.64 cm Plexiglass
SEE DETAIL A
TEFLON STOPCOCK
NOTE: ALL JOINTS AND SEAMS CEMENTED
10.16cm
.64cm
1.27cm
4.45 cm
.64cm
.79 cm
DETAIL A

Figure 3. Design details of leaching column

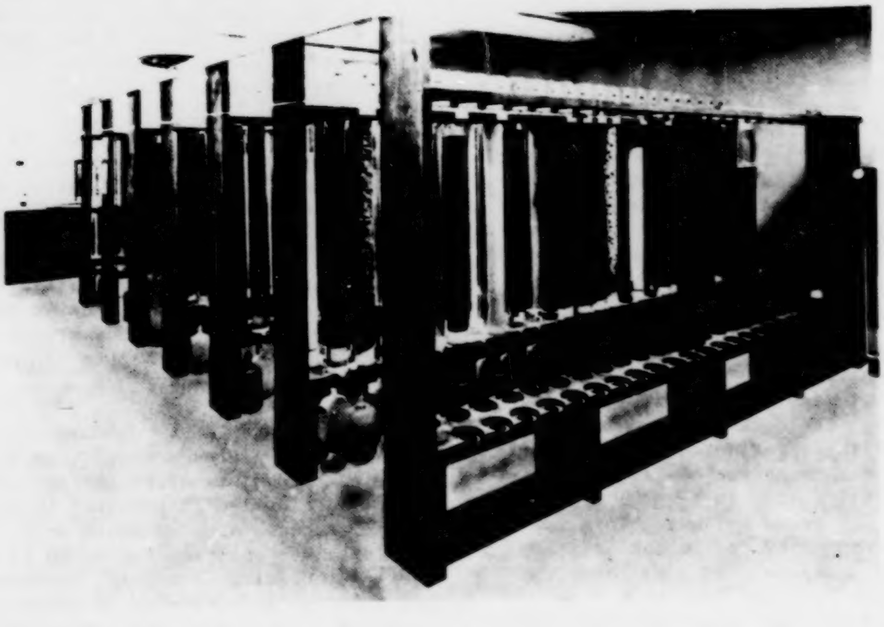


Figure 4. View of racks holding leaching columns

TABLE 2. METHOD OF ANALYSIS AND LIMITS OF DETECTION OF LOW AND HIGH LEVEL ANALYSIS OF CATIONS

Cation	Flame AA Detection Limit (mg/ℓ)	Heated Graphite Atomizer AA Detection Limit (mg/ℓ)
As	2.0	0.005
Be	0.05	0.005
Ca	0.2	*
Cd	0.05	0.003
Cr	0.5	0.003
Cu	0.2	0.003
Fe	0.3	0.003
Pb	1.0	0.002
Mg	0.02	*
Mn	0.1	0.002
Ni	0.3	0.005
Se	1.0	0.005
Zn	*	0.014

* Not used.

into conveniently handled pieces and placed in the column. The fixed sludges that had been cast into cylinders were placed in the columns and polypropylene pellets were packed around the cylinders. The variations in column loading procedures were made to accommodate those processors (A and C), who required their samples to be tested as a monolithic mass rather than as fragmented or ground material. In each case, the processor felt that the material, as packed in the columns, reflected the way the material would be placed in a landfill.

The leaching liquid used in this test was deionized, distilled water saturated with carbon dioxide. The pH of this solution is approximately 4.5. The liquid flow through the columns was maintained in a range which approximated the range of percolation through the covering material on a landfill in the eastern U. S.; 7 to 70 ml/day for these columns. This is equivalent to an hydraulic conductivity of 10^{-5} to 10^{-6} cm/sec. In some cases the natural flow rate was less than this amount, and in other cases the flow rate varied unpredictably. If the natural flow rate was lower than desired, the natural rate was allowed to regulate the flow. If the flow was too rapid, the stop-cock was used to control the flow. If the flow rate was variable, leachate was collected until 4.5 ℓ had passed through the column; then, the flow of leachate was shut off.

Samples of leachate from the columns were preserved by adding nitric acid to lower the pH to 2.0. A detailed discussion of analytical procedures is presented in a previously published report (2). All chemicals used were reagent grade. An analytical quality control program including blank corrections, spiked samples and extreme standards was incorporated into all phases of the experiment.

RESULTS

The complete data set from this experiment consists of 16 leachate samples from each of the 15 leaching columns. Each leachate sample, if of sufficient volume, was analyzed for up to 24 parameters including 13 metals, 6 anions, and 5 other parameters such as conductivity and pH. These data are summarized and discussed in three different ways. The highest single value in any single sample for each parameter is given as the worst-case estimate of the maximum level of that constituent that might be encountered. A second viewpoint is presented by the "overall" level of the parameter which is calculated as if all leachate samples from each column were pooled and a single analysis performed (total ml leached/total litres of leachate). This value gives an estimate of the long-term effects of the leachate on surrounding environment.

Neither of these calculations take into account differences in the amount of actual dry sludge solids loaded into each column; and as can be seen in Table 1, a considerable variation in the amount of dry sludge solids in each column occurred. Some solidification processes had a small amount of dry sludge solids in their final treated product. Therefore, a third presentation, the total amount and percent of each constituent leached from each column, is calculated. This calculation is made only for the high-precision columns to minimize the effects of the samples which were below detection limits (values below detection limits were set equal to zero).

Levels of constituents found in nitric acid digests of the two sludges used in this study are given in Table 3. Both are low calcium sludge (less than 2 percent) and have relatively high levels of several toxic metals. The low percent recovery for the Ni-Cad battery sludge constituents may reflect high levels of sodium and nitrate, parameters which were not included in the analysis.

Leaching Patterns

A typical difference between the leaching patterns of treated and untreated sludge columns is illustrated in Figure 5 for leachate conductivity. This is a relative measure of the ionic strength of the leachate. Leachates from the treated sludge columns show high initial values which rapidly drop to lower, fairly constant levels as the experiment progresses. The highest conductivity is found in the initial leachate sample from the column containing Ni-Cad battery sludge treated by Process B. Leachate conductivities from Process A treated sludge show the same general patterns but at lower conductivity levels. The leachate conductivity from the untreated samples of the same sludge begin and remain high and relatively constant over the same time span. The same overall pattern is also evident in leachates from the pigment production sludge. These high initial values of conductivity may represent the soluble materials from a surface wash of the solidified/stabilized sludges, while the untreated sludges continue to release high concentrations of the soluble constituents throughout the experiment.

The relatively low permeability of the untreated sludges restricted the flow of leachate through these columns so that many of the leachate samples were too small for a complete analysis to be made. The treated sludges, even though having similar low permeability, were surrounded by polypropylene beads which allowed free flow of liquid through them, larger leachate samples, and consequently, more complete analyses. This also may have only allowed a surface wash of the treated sludges where the leachate completely permeated the untreated sludges.

The curve for magnesium concentration in leachate from pigment production sludge treated by Process B (Figure 6) is typical of the leaching pattern of most constituents from the treated sludge column--a high initial value followed by a rapid decline to a rather constant lower value. However, other constituents in the same leachate samples from the same column may have very different leaching patterns. Such a case is illustrated by the concentration curve for calcium concentrations in the same leachate samples also shown in Figure 6. Calcium concentrations, in this case, start out very low, slowly increase for several months, and then slowly decline. The low initial calcium values are probably caused by common ion effects with magnesium and monovalent cations, both of which are present in high concentrations in the early leachate sample. An even more dramatic increase in calcium concentration is seen in the curve for leachate samples from the Ni-Cad battery sludge treated by Process B. A similar cause may be responsible in that the calcium increase takes place during the rapid decrease in leachate conductivity seen for this same sludge in Figure 5. Evidently, the high levels of monovalent cations reduce the solubility of calcium salt in early leachate samples. This kind of interaction between leaching rates of different constituents presents a major

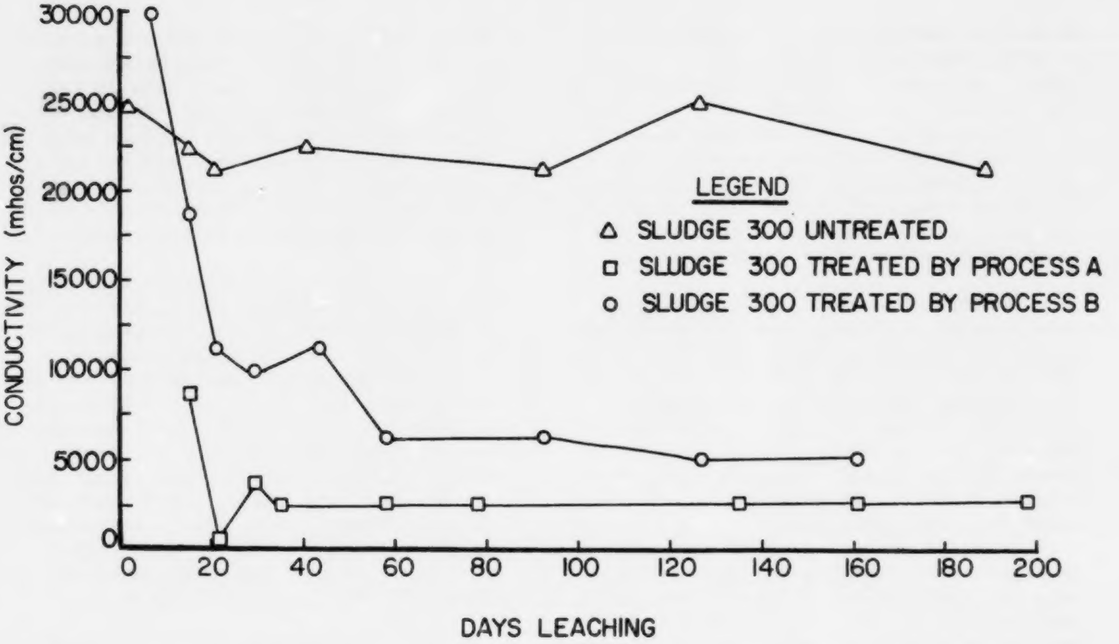


Figure 5. Plot of conductivity of leachate from treated and untreated Ni-Cad battery sludge

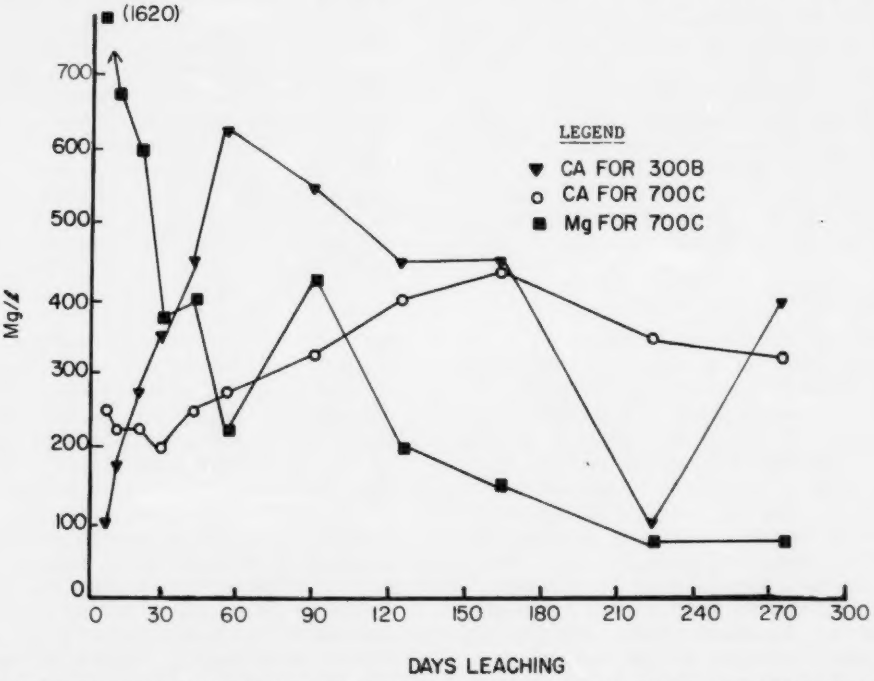


Figure 6. Concentration of calcium and magnesium by days of column leaching for Ni-Cad battery sludge treated by process B (300B) and for pigment production sludge treated by process C (700C)

TABLE 3. CONSTITUENTS IN NITRIC ACID DIGEST OF NI-CAD BATTERY AND PIGMENT PRODUCTION SLUDGES

	Mg/Kg in Dry Sludge Solids	
Constituent	Ni-Cad Battery Sludge	Pigment Production Sludge
As	BDL*	170
Be	12.9	BDL
Ca	24,300	19,000
Cd	4,640	6,350
Cr	151	86,500
Cu	322	6,950
Fe	6,260	68,500
Hg	4.49	57.0
Mg	1,070	27,300
Mn	170	2,590
Ni	169,000	1,410
Pb	102	115,000
Zn	1,440	3,280
Cl	112,000	491,000
SO_4	BDL	160,000
Si	19,390	167,000
% recovery	34	114

* BDL = below detection limits.

problem to the interpretation of short-term elutriate testing methods.

Overall and Highest Leach Concentrations

The overall and highest levels of those constituents which are generally present in amounts above the high precision analyses detection limits are shown for the Ni-Cad battery sludge in Table 4 and for pigment production sludge in Table 5. Results from the three columns used for each of the untreated and treated sludge samples and the mean of the three values are given. Those treatment means which were found to be significantly different from the untreated sludge column (control) means at the 95 percent confidence level are indicated by an asterisk in the table. The statistical test used was a one-way analysis of variance with five degrees of freedom.

Both the highest and average volumes of the leachate samples reflect the low permeability of the untreated control column; treated sludge columns produce leachate samples that averaged 2.5 to 3 times larger than those control columns. The largest leachate samples collected from the untreated control columns were well below the 4.5 ℓ maximum sample size. The pH of the leachate from the control columns and Process B columns were not significantly different, but those samples from Process A columns had significantly lower pH values (by 2.5 to 3 units).

The level of constituents lost to the leachate from the untreated Ni-Cad battery sludge columns is very low considering the nature of the sludge. The overall and highest concentrations of constituents in the leachate exceeds drinking water standards (4) only for mercury, manganese, and selenium. The overall and highest concentrations of

TABLE 4. OVERALL AND HIGHEST VALUES OF SELECTED PARAMETERS FROM ALL LEACHING COLUMNS CONTAINING NICKEL-CADMIUM BATTERY SLUDGE

Leachate Parameter		Untreated Sludge Columns				Process A Columns				Process B Columns			
		Low Precision	Low Precision	Hi Precision	Mean	Low Precision	Low Precision	Hi Precision	Mean	Low Precision	Low Precision	Hi Precision	Mean
Vol	Average	1.19	1.21	0.86	1.08	2.65	2.49	2.62	2.58*	3.14	3.02	3.24	3.13*
	Largest	3.75	2.98	2.55	3.09	4.5	4.5	4.5	4.5*	4.5	4.5	4.5	4.5*
pH	Overall	10.6	11.4	11.5	11.2	8.2	8.4	8.8	8.5*	10.5	10.9	11.0	10.8
	Highest	12.4	12.4	12.4	12.4	9.6	9.6	10.1	9.8*	12.9	12.7	12.6	12.7
COND	Overall	14600	19400	19700	17900	6560	3000	2780	4110*	5940	7180	7450	6860*
	Highest	27000	29000	24800	26900	10000	9000	9000	9300*	28900	28000	30000	20600
As	Overall	0.068	0.009	0.005	0.027	0.009	0.015	0.010	0.011	0.005	N	BDL	N
	Highest	0.300	0.028	0.012	0.110	0.032	0.100	0.024	0.052	0.012	0.008	0.003	0.008
Ca	Overall	1.4	1.4	0.95	1.2	375	443	302	373*	248	317	225	263*
	Highest	2.0	2.0	1.70	1.9	1300	1490	1280	1360*	464	579	618	554*
Cd	Overall	B	B	0.010	B	0.09	0.19	0.043	0.107	B	B	0.002	B
	Highest	0.09	0.05	0.050	0.06	0.15	0.57	0.226	0.315	B	B	0.008	B
Cu	Overall	0.048	0.036	0.013	0.032	N	N	0.012	N	N	N	0.004	N
	Highest	0.056	0.049	0.080	0.062	0.060	0.058	0.076	0.064	0.024	0.050	0.025	0.033*
Mg	Overall	B	B	0.610	B	2.25	2.35	1.13	1.91	B	B	0.022	B
	Highest	0.60	0.60	1.20	0.80	7.70	7.10	4.70	6.50*	0.10	0.10	0.100	0.10*
Ni	Overall	0.7	0.4	0.314	0.47	B	0.3	0.024	0.162	B	B	0.012	B
	Highest	2.3	0.6	2.90	1.93	0.4	1.3	0.111	0.60	B	0.35	0.130	0.24
Cl	Average	N	N	35.1	N	110	139	8.79	86	47	119	13.3	60
	Highest	250	170	704	375	400	562	32.0	331	102	459	87.0	216
SO_4	Overall	N	N	109	N	1400	1365	499	1090	N	11	4.69	7.8
	Highest	N	N	245	N	1675	1780	1300	1535	9.0	21	15.0	15

NOTE: All values in mg/ℓ except volume (in ℓ) and conductivity (in mhos/cm) and pH; B = below detection limits; N = insufficient data.

*Mean is significantly different from untreated control columns at 5% confidence level (see text).

TABLE 5. OVERALL AND HIGHEST VALUES OF SELECTED PARAMETERS FROM ALL LEACHING COLUMNS CONTAINING PIGMENT PRODUCTION SLUDGE

Leachate Parameter		Untreated Sludge Columns				Process C Columns			
		Low Precision	Low Precision	Hi Precision	Mean	Low Precision	Low Precision	Hi Precision	Mean
Vol(ℓ)	Overall	0.88	0.66	0.92	0.82	2.17	2.52	2.21	2.33*
	Highest	2.75	2.55	3.02	2.77	3.08	4.5	3.37	3.75
pH	Overall	8.0	7.6	8.0	7.9	6.1	4.9	5.5	5.5*
	Highest	8.4	8.5	8.4	8.5	7.2	5.8	6.4	6.5*
COND	Overall	8,510	8,380	8,340	8,400	N	4,000	5,530	4,760
	Highest	9,600	10,000	10,200	9,900	N	8,500	14,700	11,600
Ca	Overall	517	515	492	516	348	235	309	297.*
	Highest	731	759	599	696	499	398	450	449.*
Cd	Overall	0.75	0.82	0.914	0.83	31.6	36.5	40.10	36.0*
	Highest	1.50	1.29	1.430	1.41	57.9	54.0	96.9	69.6*
Cr	Overall	0.3	B	0.116	0.2	0.5	21.6	5.47	9.19
	Highest	1.2	1.0	0.999	1.1	1.3	80.0	20.0	33.7
Cu	Overall	0.5	0.8	0.528	0.6	0.6	4.6	2.62	2.6
	Highest	0.7	1.4	0.700	0.9	1.6	9.5	16.00	9.0
Mg	Overall	638	736	720	698	731	267	394	464
	Highest	1,012	937	1,050	1,000	3,390	545	1,620	1,851
Mn	Overall	1.6	1.9	1.83	1.8	26.1	26.9	22.5	25.2*
	Highest	2.5	2.9	2.80	2.7	38.1	85.0	77.0	66.7*
Ni	Overall	0.3	0.4	0.310	0.3	1.6	2.4	1.96	2.0*
	Highest	0.8	0.8	1.210	0.9	3.4	4.0	5.70	4.3*
Pb	Overall	1.2	1.3	0.872	1.3	2.1	1.9	1.038	1.7
	Highest	2.3	2.0	2.300	2.2	3.5	3.8	4.200	3.8*
Zn	Overall	B	B	0.050	B	12	11	7.370	10.
	Highest	B	B	0.092	B	40	20	30.00	30.
Cl	Overall	N	N	211	N	31	20	17.	23
	Highest	260	260	266	262	51	51	51.	51*
SO_4	Overall	6,930	4,430	8,330	6,563	4,660	3,380	3,670	3,903
	Highest	11,000	7,000	14,200	10,733	12,890	4,225	15,500	10,871
COD	Overall	N	N	N	N	5,610	4,225	N	4,918
	Highest	N	N	N	N	6,822	5,234	6,900	6,319

NOTE: All values in mg/ℓ except volume (ℓ), conductivity (mhos/cm), and pH;
B = below detection limits; N = insufficient data.
* Mean is significantly different from untreated control at 95% confidence level (see text).

calcium, chloride, and sulfate are also extremely low. Other constituents for which only the highest concentrations exceeded drinking water standards were arsenic and cadmium. The high conductivity seen for these leachates must be indicative of large amounts of sodium and nitrate which is present in the sludge. The leachate from untreated pigment production sludge, on the other hand, exceeds the drinking water standards for both overall and highest concentrations of cadmium, chromium, mercury, manganese, lead, and sulfate (Table 5). These leachate samples also showed high levels of calcium, magnesium and sulfate. The relatively low loss rates from the untreated sludges probably reflects their low permeability and low pH. The bulk of the heavy metal sulfides and hydroxides have very low solubilities at high pH's.

The solidification/stabilization process used to treat the Ni-Cad battery sludge significantly effected only the levels of calcium, the highest values of magnesium, and in one case, the highest concentration of copper found (Table 4). The levels of calcium in the leachate from the processed sludges are over 200 times higher than calcium levels in the untreated sludge leachates. These high calcium levels must be caused by calcium added in the treatment reagents (e.g., lime and cement) since the original Ni-Cad sludge is relatively low in calcium content. Appreciable amounts of magnesium must be present in flyash or "lime additive" used by Process A; but absent in the reagents used by Process B since leachates from Process A-treated sludges had significantly higher, and from Process B treated sludges significantly lower, magnesium levels. Process B also significantly lowered the amount of copper in leachate from this sludge.

Other trends found in the leaching data from treated and untreated Ni-Cad battery sludges are higher losses of cadmium and sulfate from Process A, and lower levels of nickel and sulfate from Process B-treated sludges. Several differences also occurred in leachate losses of other parameters which are present in concentrations below the low precision detection limits. The overall and highest leachate concentrations of these constituents as determined for the high precision columns only are given in Table 6. Leachate from the column containing Ni-Cad battery sludge treated by Process A had higher overall and highest concentrations than did leachate in the control columns for beryllium, chromium, manganese, selenium, zinc, and cyanide. Of these, only chromium and zinc were above the drinking water standards. Process B produced leachates with higher chromium, lead, and cyanide, with only lead exceeding drinking water standards.

Treatment of pigment production sludge by Process C (Table 5) significantly increased the rate of loss of cadmium (by 40-50 times), manganese (by 14-25 times), and nickel (by 5-7 times). Although not significant statistically, higher rates of loss from the treated sludge columns also were found for chromium (by 30-45 times), copper (by 4-10 times), and zinc (by at least 100 times). Significantly lower amounts of calcium (about 1/2) and chloride (about 1/5) were also lost from Process C-treated pigment production sludges. Sludge treated by Process C had higher overall concentrations of seven, and larger "highest" values of nine, of the parameters tested.

Percent of Major Constituents Leached

Calculation of the percent of each constituent leached from the columns over the length of the study gives an estimate of constituent loss rates which takes into account the different amounts of dry sludge solids loaded into each column. If the evaluation was based only on concentrations, those processes which added the largest amount of treatment reagents, and therefore the least sludge solids, would be given an advantage over processes with high proportions of dry sludge solids in their final product. The weight of dry sludge solids loaded into each column was given in Table 1. Percent of each constituent leached is calculated by summing the product of the volume of each sample (ℓ) times the concentration of that constituent in the sample (mg/ℓ) to give the total amount leached (mg); this value is then divided by the amount of the constituent in the dry sludge solids which were loaded into the column (using sludge composition data in Table 3) and multiplied by 100 to give a percentage value. The results of these calculations are given for Ni-Cad

TABLE 6. OVERALL AND HIGHEST VALUES OF CONSTITUENTS OF LOW CONCENTRATION FROM HIGH PRECISION COLUMNS CONTAINING NI-CAD BATTERY SLUDGE

Constituent	Untreated Sludge Columns		Process A Column		Process B Column	
	Overall	Highest	Overall	Highest	Overall	Highest
Be	N*	0.0002	0.0040	0.0470	N	0.0004
Cr	0.001	0.004	0.018	0.099	0.010	0.047
Hg	0.0110	0.0570	N	0.0003	N	0.0038
Mn	0.006	0.122	0.061	0.922	0.002	0.016
Pb	0.003	0.019	0.003	0.026	0.052	0.899
[illegible]	0.006	0.020	0.010	0.073	N	0.003
Zn	0.006	0.050	0.134	1.640	0.009	0.070
Cu	0.002	0.010	0.015	0.110	0.024	0.140

* N = no or insufficient data.

battery sludge in Table 7 and pigment production sludge in Table 8.

Less than 1 percent of all constituents for which analyses were made were lost from the columns containing untreated Ni-Cad battery sludge. A very small fraction of the dry sludge solids were removed from the column over the period of the study. Both treatment processes are seen to have similar but generally higher percent loss values reflecting the lower amount of sludge solids in the columns. Notable exceptions are calcium from both processed-sludge columns and magnesium from the Process A columns. These higher losses probably reflect the addition of calcium (and perhaps magnesium) in the treatment reagents which are intentionally not included in these calculations. The "treatment" actually increased the total amount of calcium in the waste. The column containing the Ni-Cad sludge treated by Process A lost a higher percentage of all constituents analyzed except arsenic and nickel (which were below detection limits), and mercury. The column containing sludge processes by B lost higher proportions of all constituents analyzed except arsenic, cadmium, mercury, magnesium, nickel, selenium, and sulfate.

The total loss of selected constituents from the column containing untreated pigment production sludge was also less than 1 percent except for calcium, magnesium and sulfate (Table 8). About 7.5 percent of both calcium and magnesium, and about 15 percent of the sulfate in the sludge were lost from these columns. The higher rate of loss of these constituents from the pigment production sludge may reflect their higher solubility in the lower pH of this leachate (8.0) than in the untreated Ni-Cad battery sludge leachate (11.5), and the lower amount interfering, monovalent ions present in the sludge. Process C was unsuccessful in lowering the percent of any of the cations lost to leaching waters in this experiment--cadmium, chromium, copper, manganese, nickel, and zinc being lost over 30 times the proportion lost by the control sludges. Between two and three times the percentage of sulfate was lost from the treated sludge, but only about half the percentage of chloride.

DISCUSSION AND CONCLUSIONS

The industrial waste sludges used in this study have the potential of being serious threats to surface and groundwaters. Although both sludges lost heavy metals to leaching waters in appreciable amounts, the rate of metal release from the sludge appears to be limited by their solubility at the basic pH of the sludges and the low permeability of the untreated

TABLE 7. TOTAL AMOUNT AND PERCENT OF EACH CONSTITUENT LEACHED FROM HIGH PRECISION COLUMNS CONTAINING NI-CAD BATTERY SLUDGE

	Untreated Sludge Column		Process A Column		Process B Column	
Constituent	Total mg Leached	% Leached	Total mg Leached	% Leached	Total mg Leached	% Leached
As	2.1	B*	0.28	B	0.008	B
Be	<0.001	<0.001	0.16	0.69	0.001	0.002
Ca	159.	0.11	11,800	27.3	10,700	13.5
Cd	0.10	<0.001	1.7	0.02	0.089	<0.001
Cr	0.013	0.001	0.724	0.27	0.47	0.096
Cu	0.137	0.007	0.48	0.083	0.197	0.019
Hg	0.12	0.42	0.002	0.025	0.021	0.143
Mg	6.3	0.096	44.0	2.3	1.1	0.031
Mn	0.061	0.006	2.4	0.79	0.091	0.016
Ni	3.20	<0.001	0.93	<0.001	0.56	<0.001
Pb	0.029	0.005	0.118	0.066	2.5	0.74
Se	0.061	N*	0.372	N	0.008	N
Zn	0.060	0.001	5.2	0.20	0.43	0.009
Cl	363	0.051	351	0.17	633	0.16
CN	0.02	N	0.58	N	1.15	N
SO_4	42,200	N	19,500	N	223	N
SO_3	33	N	10	N	94	N
Avg. pH	11.5		8.9		11.0	

* B = constituent below detection limits in sludge analysis;
N = constituent not determined in sludge analysis.

sludges. Over the 2 year leaching period of this study, less than 1 percent of the heavy metals was found in the leachate. The loss of toxic metal apparently would continue at these levels for many years. The Ni-Cad battery sludge also appears to be releasing high concentrations of soluble constituents which also continued over the length of the experiment.

The solidification/stabilization techniques used in this experiment had variable effects upon pollutant containment for the sludges. Process B, the soluble silicate and cement additive procedure, reduced the amount of metals in the leachate to the greatest degree. Sludge treated by this process, however, had the highest initial conductivity levels indicating a large immediate loss of soluble constituents. Process A, using flyash and lime, on the other hand had very little effect upon the rate of loss of metals but did appreciably lower the initial and long-term loss of soluble constituents as indicated by lower conductivity levels. The loss of soluble constituents parallels the amount of surface area exposed--the Process B product being broken into chunks with relatively higher surface area (and conductivity values) than the monolithic Process A product. Process B, however, even with a greater surface leaching area, must have a much greater containment ability due to its higher pH and silicate additives.

Process C, the urea-formaldehyde resin product, appears to be counter productive to the containment of the metal species in the sludge. The acidified solution necessary for the polymerization

TABLE 8. TOTAL AMOUNT AND PERCENT OF SELECTED CONSTITUENTS LEACHED FROM HIGH PRECISION COLUMNS CONTAINING PIGMENT PRODUCTION SLUDGE

Constituent	Untreated Sludge Column Total mg Leached	 % Leached	Process C Column Total mg Leached	 % Leached
As	0.080	0.010	0.049	0.020
Be	0.070	B*	1.2	B
Ca	6,800	7.4	7,514	27.4
Cd	12.6	0.041	974	10.6
Cr	1.5	<0.001	133.	0.12
Cu	7.3	0.022	63.	0.64
Hg	0.062	0.023	0.17	0.21
Mg	9,960	7.5	9,600	24.4
Mn	25.4	0.20	546	14.6
Ni	4.3	0.063	47.5	2.3
Pb	12.6	0.002	25.2	0.015
Se	0.15	N*	N	N
Zn	0.70	0.004	179.	3.8
Cl	2,900	0.12	415	0.059
SO_4	115,000	14.9	89,100	38.6
Avg. pH	8.0		5.6	

* B = constituent below detection limits in sludge analysis;
N = constituent not determined in sludge analysis.

reaction apparently serves to solubilize many of the contained metals increasing their rate of loss from the treated sludge. The smaller surface area of the treated sludge does, however, lower the long-term loss of soluble constituents as measured by conductivity.

Calculation of the percent of each constituent lost from the column shows that a very low proportion of most constituents were lost from the leaching columns over the length of this study. Sludges treated by Processes A and B lost a greater proportion of all constituents measured (except mercury and nickel for both and magnesium for Process B). Process C treated sludges lost much greater percentages of all constituents measured except chloride. Thus, when calculated on a sludge basis, the small benefits of solidification/stabilization largely disappeared in this experiment.

Assessment of contaminate loss from treated and untreated sludges using small-column, long-term, submerged leaching procedures confirms the pollutant potential of these sludges. The treatment processes used in this study did not appear to increase the containment of toxic metals. Further studies using other experimental methods should be undertaken.

ACKNOWLEDGEMENT

This study was part of a major research program on the chemical fixation technology, which is now being conducted by the U. S. Army Engineer Waterways Experiment Station and funded by the Environmental Protection Agency, Municipal Environmental Research Laboratory, Solid and Hazardous Waste Research Division, Cincinnati, Ohio under Interagency Agreement, EPA-IAG-D4-0569. Robert E. Landreth is the EPA Program Manager for this research area.

References

1. Bartos, M. J., Jr., and M. R. Palermo. 1977. Physical and Engineering Properties of Hazardous Industrial Wastes and Sludges. EPA-600/2-77-139. U. S. Environmental Protection Agency, Cincinnati, Ohio. 89 pp.

2. Maloch, J. L., D. E. Averett, and M. J. Bartos, Jr. 1976. Pollutant Potential of Raw and Chemically Fixed Hazardous Industrial Waste and Flue Gas Desulfurization Sludges. EPA-600/2-76-182. U. S. Environmental Protection Agency, Cincinnati, Ohio. 117 pp.

3. Malone, P. C., R. B. Mercer, and D. W. Thompson. 1978. The Effectiveness of Fixation Techniques in Preventing the Loss of Contaminants from Electroplating Wastes. In: First Annual Conference on Advanced Pollution Control for the Metal Finishing Industry. EPA-600/8-78-010. Industrial Environmental Research Laboratory, U. S. Environmental Protection Agency, Cincinnati, Ohio. pp 130-143.

4. National Academy of Sciences, National Academy of Engineering, Water Quality Criteria, 1972. A Report of the Committe on Water Quality Criteria, EPA-R-73-033, U. S. Environmental Protection Agency, Washington, D. C. 1973. 594 pp.

5. Thompson, D. W., P. G. Malone, and L. W. Jones. 1979. Survey of Available Stabilization Technology. In: Toxic and Hazardous Waste Disposal, Vol 1. R. B. Pojasek, Ed. Ann Arbor Science Publishers, Inc., Ann Arbor, Mich. pp 9-22.

ORGANIC LEACHATE EFFECTS ON THE PERMEABILITY OF CLAY LINERS

David Anderson and K. W. Brown
Texas Agricultural Experiment Station
Texas A&M University
Soil & Crop Sciences Department
College Station, TX 77843

ABSTRACT

Permeability remains the primary criterion for evaluating the suitability of clay soils for the lining of hazardous waste landfills. An evaluation of the physical classes of hazardous waste and the leachates they release indicates that clay liners could be exposed to a wide range of organic fluids. Procedures are outlined for rapidly testing the effect of organic chemicals on the permeability of clay liners. Large permeability increases were observed in two smectite clays after the soils were permeated with neutral-polar, neutral-nonpolar, and basic organic fluids.

INTRODUCTION

In the last decade, several hazardous waste disposal facilities have been identified as the source of contaminants found in nearby groundwater supplies. As a result, many states have adopted regulations that require hazardous waste landfills and surface impoundments to have clay liners with permeabilities not to exceed 10^{-7} cm/sec.

Test procedures for determining the permeability of clay liners usually are performed using a standard permeant (0.01 N $CaCl_2$ or $CaSO_4$) which may bear little resemblance to the leachate released from disposed liquids or sludges. An evaluation of the physical classes of industrial waste and the leachates they generate has indicated that clay liners could be exposed to a wide range of organic chemicals.

Procedures are given below for evaluating the permeability of compacted clay soils to leachates released from disposed liquids and sludges. The procedures are followed by a discussion of the results obtained from the testing of two smectite clay soils permeated with organic fluids.

A. PHYSICAL CLASSES OF WASTES

Wastes found in industrial disposal facilities fall into four physical classes; aqueous inorganic, aqueous organic, organic, and sludges (EPA, 1974)(Figure 1). Cheremisonoff et al. (1979) estimated that 90%, by weight, of industrial hazardous wastes are produced as liquids. These liquids are further estimated to contain solutes in the ratio of 40% inorganic to 60% organic.

"Aqueous-inorganic" is the class of wastes in which water is the solvent (dominant fluid), and the solutes are mostly inorganic. Examples of these solutes are inorganic salts, metals dissolved in inorganic acids, and basic materials such as caustic soda. Examples of wastes in this category are brines, electroplating waste, metal etching wastes, caustic rinse solutions, and spent metal catalysts.

FIGURE 1: PHYSICAL CLASSES OF WASTE

- Aqueous - Inorganic
- Aqueous - Organic
- Organic
- Sludges

"Aqueous-organic" is the class of wastes in which water is the solvent and the solutes are predominantly organic. Examples of these solutes are organic chemicals that are polar or charged, as is inferred by their water-solubility. Examples of this class of wastes are wood preserving wastes, water base dye wastes, pesticide container rinse water, and ethylene glycol production wastes.

"Organic" is that class of waste in which an organic fluid is the solvent and the solutes are the other organic chemicals dissolved in the organic solvent. Examples of this class of wastes are oil base paint waste, pesticide manufacturing wastes, spent motor oil, and spent cleaning solvents.

"Sludges" represent the fourth class of wastes. They are generated when a waste stream is dewatered, filtered, or treated for solvent recovery. Sludges are characterized by high solids content such as that found in settled matter or filter cakes and consists largely of clay minerals, silt, precipitates, fine solids, and high molecular weight hydrocarbons. Examples of this waste are API separator sludge, storage tank bottoms, treatment plant sludge, or any filterable solid from any production or pollution control process.

Both economic and pollution control pressures continue to mandate solvent recovery and other reductions in the volume of liquid waste streams. These factors have and will continue to make sludges the fastest growing class of wastes. After placement of sludges in a waste disposal facility, leachates migrate out of the sludge due to gravitational forces, overburden pressures, and hydraulic gradients. These leachates are similar in physical form to the other three classes of waste given in Figure 1.

B. LEACHATES GENERATED BY INDUSTRIAL WASTE

To determine the effect of a specific waste on the permeability of a specific clay liner, two unique leachates must be investigated. The unique leachates are the flowable constituents of the waste and the flowables generated from percolating water leaching through the waste (Figure 2).

Flowable constituents of a waste, hereafter referred to as the primary leachate, include both fluids in the waste, the solvent, and all components dissolved in these fluids (solutes). The nature of the primary leachate solvent phase depends on the composition of the waste and may be predominantly water or any organic fluid discarded by industries. Flowables generated from percolating water are composed of water (the solvent) and all components dissolved in this water (solutes). This water based mixture is hereafter referred to as the secondary leachate.

The predominant fluid or solvent phase of a leachate may be water or any organic fluid (Figure 3). Corresponding solutes in a leachate are any chemicals that dissolve in the solvent. As in the waste classification, both primary and secondary leachates are divided into a solvent, the dominant fluid component, and a solute, components dissolved in the solvent (Figure 4 and 5). While the solutes in a leachate can affect the permeability of a clay liner, the solvent phase of a leachate will usually exert a dominating influence on the liner's permeability.

Essentially all available literature on the behavior of leachates in soil relate to systems where water is the solvent phase (Goring *et al.*, 1972). Water is viewed as the carrier fluid and the organic chemicals are present in only trace quantities. However, solvent phases of a landfill leachate may be water or any of the organic fluids present in industrial waste (Figure 6). Organic fluids placed in industrial waste disposal facilities cover the spectrum of chemical species such as acidic, basic, neutral-polar and neutral-nonpolar compounds.

Organic acids are any organic fluid that has acid functional groups. The group has the potential to be very reactive with and mobile in clay liners.

Organic bases are any organic fluid capable of accepting a proton to become an ionized cation. Since these fluids are positively charged, they will adsorb strongly to clay surfaces. By adsorbing

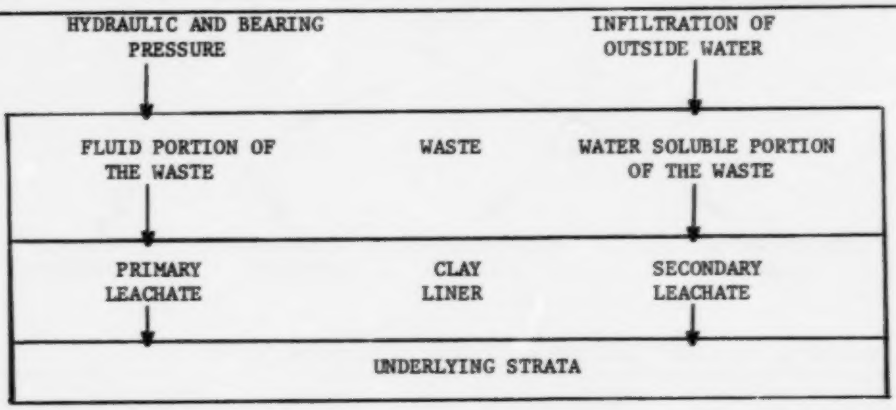

HYDRAULIC AND BEARING PRESSURE
INFILTRATION OF OUTSIDE WATER
FLUID PORTION OF THE WASTE
WASTE
WATER SOLUBLE PORTION OF THE WASTE
PRIMARY LEACHATE
CLAY LINER
SECONDARY LEACHATE
UNDERLYING STRATA

FIGURE 2. SOURCES OF LEACHATE THAT MAY COME IN CONTACT WITH CLAY LINERS

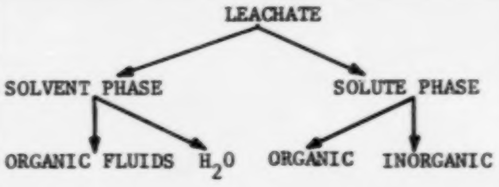

LEACHATE
SOLVENT PHASE
SOLUTE PHASE
ORGANIC FLUIDS
H_2O
ORGANIC
INORGANIC

FIGURE 3. COMPOSITION OF THE LEACHATE OF A WASTE

to the clays, these fluids have the potential for causing volume changes in clays by changing interlayer spacings, as well as by dissolving certain constituents of the clay minerals.

Neutral-nonpolar compounds are those organic fluids that have no charge and a small, if any, dipole moment. This group of fluids is further divided into aliphatic and aromatic hydrocarbons. With no charge and little dipole moment, these chemicals have the potential for moving through clay liners rapidly and eroding the pores through which they pass, thus increasing permeability. These chemicals may also increase permeability of a clay liner by displacing water from the clay liner which may in turn cause shrinkage.

Neutral-polar compounds have no charge but exhibit stronger dipole moments than the "neutral-nonpolar" organics. This group of fluids can be further divided to represent its functional group types: alcohols, aldehydes, glycols, alkyl halides and ketones. Their effect on permeability may be related to their effect on the interlayer spacing of a clay and on the surface tension of the pore water.

Water is a unique solvent in several ways. It has a strong dipole moment and a high dielectric constant. Water may cause a clay liner to shrink, swell, heave, crack or pipe. Water may also act to increase the hydraulic gradient that moves fluids in soil. While water might not be the solvent in the primary leachate of a waste, it is usually the solvent in the secondary leachate.

C. TEST METHOD FOR DETERMINING THE EFFECTS OF WASTE LEACHATE ON THE PERMEABILITY OF COMPACTED CLAY SOILS (CONSTANT ELEVATED PRESSURE METHOD)

To assess the suitability of compacted clay soils for the lining of waste disposal facilities, the primary laboratory measurement made is saturated conductivity or permeability. Permeability measurements should be made on a core of the clay soil that has been compacted at its optimum moisture content to achieve the maximum density possible for a given compactive effort. The procedure for determining soil moisture-density relations is given in the 1978 Annual Book of ASTM Standards Part 19, Test Method Number D 698-70.

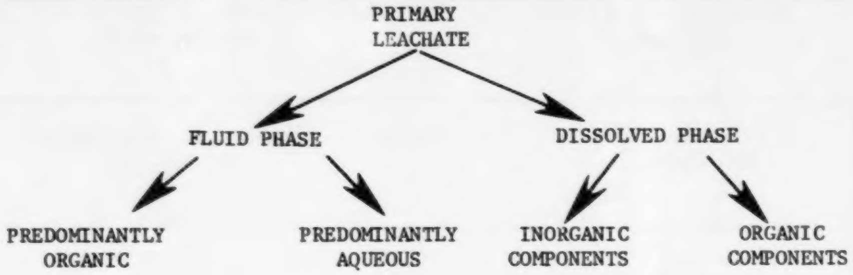

PRIMARY LEACHATE
FLUID PHASE
DISSOLVED PHASE
PREDOMINANTLY ORGANIC
PREDOMINANTLY AQUEOUS
INORGANIC COMPONENTS
ORGANIC COMPONENTS

FIGURE 4. PRIMARY LEACHATE GENERATED AT DISPOSAL SITES

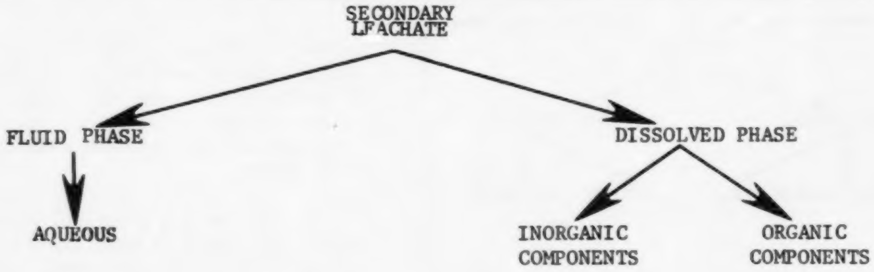

SECONDARY LEACHATE
FLUID PHASE
DISSOLVED PHASE
AQUEOUS
INORGANIC COMPONENTS
ORGANIC COMPONENTS

FIGURE 5. SECONDARY LEACHATES GENERATED AT DISPOSAL SITES

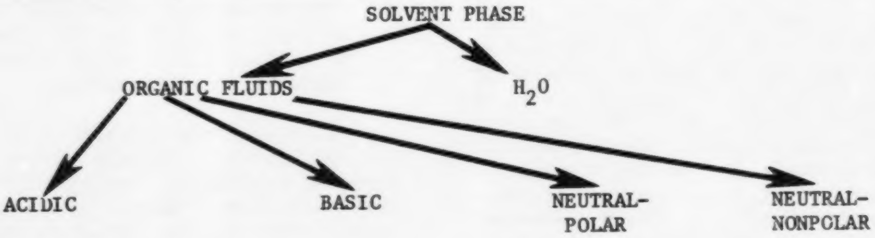

SOLVENT PHASE
ORGANIC FLUIDS
H_2O
ACIDIC
BASIC
NEUTRAL-POLAR
NEUTRAL-NONPOLAR

FIGURE 6. SOLVENT PHASE OF THE LEACHATE OF A WASTE

Clays compacted at optimum moisture content may have permeability values as low as 10^{-9} cm/sec. In addition, it may be necessary to pass one or more pore volumes of a standard leachate, .01N $CaSO_4$, to obtain a stable permeability value for the clay. For these reasons, it may be necessary to use high pressure to increase the hydraulic gradient and reduce the time length of the test (Bennett, 1966). Trapped air is a common cause for artificially low permeability values (Christiansen et al., 1946). An increase of pressure reduces air trapped in the core by increasing the weight of gas that will dissolve in water flowing through the core (Jones, 1960). The higher pressures will also reduce the volume of the remaining air pockets.

For a given waste-clay liner combination, there are two fluids that may alter the liner's permeability, the fluids present in the waste (primary leachate) and the fluids generated by water percolating through the waste(secondary leachate). The primary leachate of a waste may be obtained for permeability testing by decanting the liquids present in the waste or by collecting the filtrate from vacuum filtration of the waste. The filter cake obtained from filtration of the waste should then be shaken with an equal weight of water and refiltered. The resulting second filtrate can then be used as the secondary leachate of the waste. Enough waste should be processed in this manner to yield at least four pore volumes of primary and secondary leachate to use in the permeability tests. Two liters of each leachate should be enough to run duplicate cores with each leachate in the test procedures discussed below. Since these leachates may cover the spectrum of organic fluids, the permeameter used for testing these fluids must be capable of safely operating with industrial solvents, volatile compounds, corrosive acids and strong bases.

Tests on soils of low permeability must be carefully performed if they are to be accurate. Leaks, volatile losses, or channel flow along the interface of the permeameter and soil will greatly affect permeability values (Bowles, 1968).

To avoid channel formation, the clay is seated at low pressure. By letting 10 mm of standard leachate (.01 N $CaSO_4$) stand on the core for 24 hours, an effective seat is obtained for the top few millimeters of the clay core. This thin layer will prevent bulk flow and the rest of the core should adequately seal at elevated pressures.

In order to facilitate ease of duplication of the test apparatus, the permeameter is based on readily available and easily modified components. Figure 7 illustrates the modified compaction permeameter which is based on the standard compaction permeameter that is available through most soil testing supply houses. All components are in common with the standard permeameter except for the enlarged fluid chamber, extended studs and high pressure fittings.

For use with fluids other than water, all gaskets should be teflon. To avoid leakage around the gaskets, all metal surfaces against which the gaskets are seated should be wiped clean of grit. All components should withstand continuous operation at pressures up to 4 atmospheres.

To limit the volume for diffusive mixing of leachate samples after they have passed through the clay core, the fluid outlet should be fitted with an adapter to 1/8 inch inside diameter teflon tubing. Using translucent teflon at the permeameter's outlet provides a convenient window with which to monitor the explusion of entrapped air. Standard leachate should be passed through the permeameter until there are no air bubbles visible in the outlet tubing. If soil piping occurs, eluted soil clays will be visible either clinging to the inside walls of the outlet tubing or as a suspension in the collected flow samples.

Volatile losses may occur during sample delivery from the outlet tubing to the sample bottles in the fraction collector. To limit these volatile losses, the top of each sample bottle is fitted with a long stem funnel and the entire fraction collector is placed in an air tight cooled compartment.

The entire test apparatus should then be fitted into a vented hood. (Figure 8). This extra precaution is insurance against worker injury in case

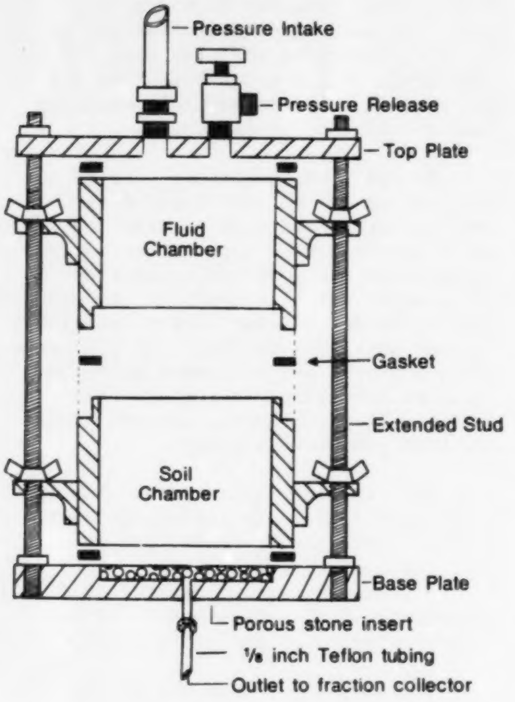


FIGURE 7. SCHEMATIC OF THE COMPACTION PERMEAMETER

of a gasket blow out. If multiple permeameters are to be used, each should have its own pressure cut-off valve to prevent the complete shut down of a test to remove a single permeameter.

With several permeameters producing leachate, it may be desirable to have an automatic leachate fraction collector. This is especially useful with long term tests.

Equipment requirements for the simultaneous testing of two wastes (2 wastes x 2 leachates (primary and secondary) x 2 replications + control permeameters = 10 permeameters) are as follows:

1. Soil crusher (C-2 Laboratory Crusher)[1]
2. Soil grinder (Hewitt Soil Grinder)[2]
3. 2 mm sieve (CB-810 Brass Sieves)[1]
4. 10 moisture cans (LT-30 Tin Sample Boxes)[1]
5. Balance capable of weighing 20 kg (L-500 Heavy Duty Balance)[1]
6. 105° C drying oven to determine water content of soil samples
7. 10 compaction molds (CN-405 Standard Compaction Mold)[1]
8. Compaction hammer (CN-4230 Mechanical Compactor)[1]
9. Steel straight edge
10. 10 permeameter bases and top plates (K-611 Permeameter Adapter)[1]
11. A source of compressed air with a water trap, regulator and pressure meter
12. An air manifold to permit simultaneous testing of 10 core samples
13. A fraction collector with automatic timer for collection of samples over time from 10 permeameters (Brinkmann Linear II)
14. An air tight, cooled chamber to limit volatile loss of samples during and after sampling
15. A vented hood to hold the compaction permeameters and chamber containing the fraction collector

Procedures are given below for the 10 permeameter test system using the equipment described above. Approximately 50 kg of the air dried clay soil will be required for each test incorporating 10 permeameters.

1. Obtain at least 100 kg of the clay soil (CS) to be tested. Break the CS down to golf ball size clods and lay them out to air dry.

---

[1] Soil Test Inc.

[2] Robert B. Hewitt Welding and Repair (815-269-2030). Danforth, Illinois 60930.

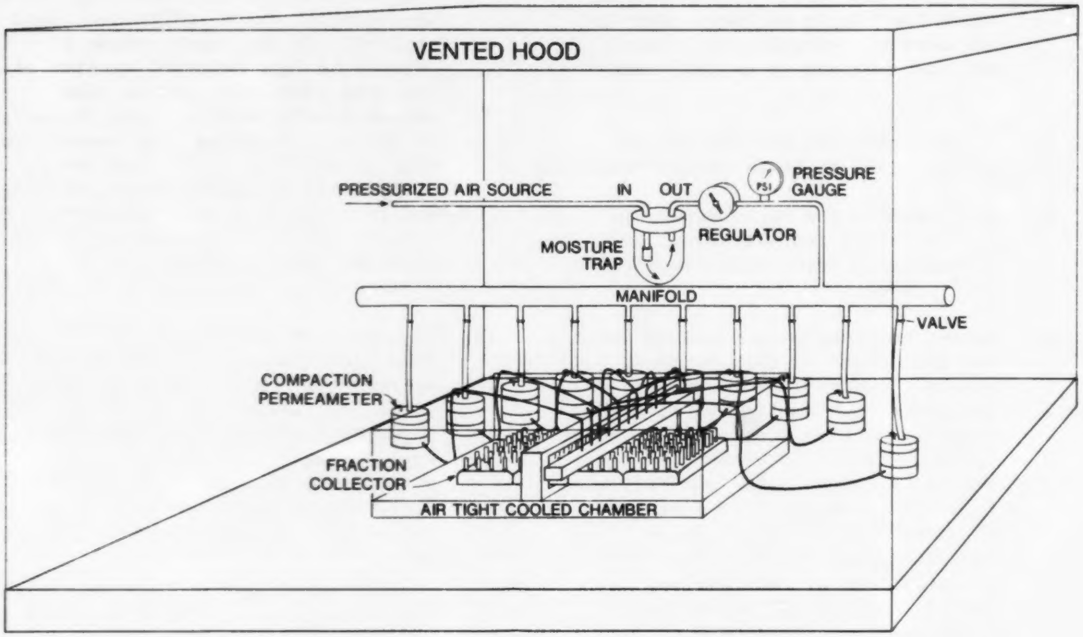


FIGURE 8. SCHEMATIC OF THE COMPACTION PERMEAMETER TEST APPARATUS IN A VENTED HOOD

2. Grind the air dried CS and pass it through a 2 mm sieve.

3. Mix the sieved CS thoroughly and divide it into two lots. Each lot of CS should be placed in air tight containers and stored at room temperature until their time of use. Each lot should be enough CS to prepare 10 compaction molds. (Fifty kilograms will provide for some spillage losses assuming a mold volume of about 1,000 cm3).

4. Use one lot of the CS to determine the moisture density relations of the CS by following the ASTM Method D-698-70*. This will determine the CS's optimum moisture content to obtain the maximum density at the compactive effort to be used.

5. Use the second lot of CS to prepare 10 compaction molds at optimum moisture content.

6. Fit a valve on top of the permeameter top plate with pressure fittings and connect it to a source of air pressure via copper tubing. Place a water trap, pressure regulator and pressure gauge in line between the air pressure source and the permeameter. The water trap should be located between the pressure source and regulator to prevent build up of debris on the membrane in the regulator. The pressure gauge should be located between the regulator and a pressure manifold to the 10 permeameters so that the hydraulic head being exerted on the clay cores may be monitored.

7. Pass at least one pore volume of the standard leachate (.01 N $CaSO_4$ or $CaCl_2$) through the clay cores. After the permeability values are stable and below 10^{-7} cm/sec , release the pressure, disassemble the permeameter and examine the core.

8. If the clay core has shrunk, it is unsuitable as a clay liner.

9. If the clay has expanded out of the mold, remove the excess with a

---

[*] This method can be found in the 1978 Annual Book of ASTM Standards Part 19.

straight edge while trying not to smear the clay's surface. Reweigh the core to determine its density and then remount it on the permeameter.

10. If the clay has not changed its volume, remount it on the permeameter.

11. Repressurize the permeameter and pass standard leachate until the permeability value stabilizes below 10^{-7} cm/sec.

12. Remove the remaining standard leachate from eight of the ten fluid chambers and replace it on four of the cores with duplicates of the primary leachate from the two wastes to be tested. The other four cores should be tested using the filtrate from well shaken 1 to 1 mixtures of water and the wastes to be tested. Thus, one test run (10 cores) is sufficient to maintain two control cores while evaluating the permeability of duplicate cores treated with the primary and secondary leachate of two different wastes.

13. If after passage of one pore volume of the various leachates, the permeability values of the cores are still below 10^{-7} cm/sec disassemble the permeameter and reexamine the cores.

14. If the clay core has shrunk, it is unsuitable as a clay liner for that waste.

15. If the clay has not changed volume or has expanded, remount it on the permeameter.

16. Repressurize the permeameter and pass volume of the standard leachate. If its permeability has climbed above 10^{-7} cm/sec , the clay is not suitable for containing the waste. If the permeability values measured on a waste's primary and secondary leachate have consistently stayed below 10^{-7} cm/sec , proceed to step 17.

17. Examine the translucent teflon outlet tube for signs of soil particle migration out of the core. If there is evidence of soil migration, pass at least one more pore volume to observe if this internal erosion of the core continues. If it does continue after the two pore volumes of standard leachate have passed, the clay is unsuitable for that waste. If the soil migration stops, at least one pore volume of the standard leachate should be passed to assure that the core stabilization is permanent and then proceed to step 18.

18. If there are no signs of soil migration, depressurize the system and extrude the clay cores from their molds to examine them carefully for signs of cracking, internal erosion, soil piping, clay dissolution, structural changes, or any other difference from the control cores (those having received only standard leachate).

If there are no signs the cores have deteriorated, the clay should be suitable for lining the disposal facility to contain that waste.

Permeability (K) of the clay soils can be calculated using the following formula:

$$K = \frac{V\,L}{A\,t\,(L + H)}$$

K = permeability (cm/sec)
V = volume of flow (cm^3) in time (t)
A = cross-sectional area of flow (cm^2)
t = time (sec.)
L = length of soil core (cm)
H = pressure (cm of H_2O)

The sign is negative to indicate the direction of flow.

D. PERMEABILITY OF TWO SMECTITE CLAY SOILS PERMEATED WITH ORGANIC FLUIDS

Two smectite clay soils that are typical of those used to construct clay liners were selected for use in the evaluation of the developed test procedures. Table 1 lists physical and chemical properties for those soils. Smectite clay minerals are composed of expandable lattices and therefore exhibit a large capacity for shrinking and swelling.

TABLE 1. PHYSICAL AND CHEMICAL PROPERTIES OF TWO SMECTITIC CLAY SOILS

Soil Name	% Clay	% O.M.	CEC	Exc. Ca	Exc. Na
			meq/100g		
Lufkin	48	1	24	18	3
Houston Black	56	3	36	saturated	<1

Of the two clay soils, Houston Black has the highest amount of clay sized particles, organic matter, and cation exchange capacity. Houston Black, which developed over a limestone bedrock, is approximately 33% by weight calcium carbonate. Consequently its cation exchange sites are essentially saturated with calcium.

Lufkin clay has a substantially larger percentage of its cation exchange sites occupied by sodium ions than does the Houston Black clay. Consequently, of the two clay soils studied, the Lufkin clay has the larger potential for shrinking and swelling.

Table 2 lists physical and chemical properties of the permeants used in this study. Fluid types were selected from each of the four classes of organic leachates described in Section B and generated by the "organic" and "sludge" waste classes described in Section A.

All test procedures were performed as described in Section C. In the place of actual leachates, reagent grade organic fluids were used as the test permeants. Results of these permeability tests are given in Figures 9-11.

Acetic acid (Figure 9) caused decreases in the permeability with both Houston Black and Lufkin. However, there was a significant amount of soil piping occuring in the two acid permeated cores as was evidenced by the presence of soil particles in the leachate. Both acid dissolution and soil piping have been discussed by these authors as possible failure mechanisms for clay liners (Brown et al., 1980).

Aniline (Figure 9) treated cores both showed substantial permeability increases. Permeability increased nearly 100 fold for Lufkin clay over that obtained with water. Permeability of the Houston Black core increased approximately 10 fold.

Acetone (Figure 10) treated cores showed an initial decrease followed by large increases in permeability. Lufkin and Houston Black clays exhibited 1,000 fold and 50 fold increases in permeability respectively.

Ethylene glycol (Figure 10) cores showed 100 fold and 4 fold increases in permeability with the Lufkin and Houston Black clays respectively. Interestingly, the ethylene glycol treated Houston Black core showed a steady decrease in permeability following the initial permeability increase.

Both xylene and heptane (Figure 11) treated cores showed substantial permeability increases. Xylene treated cores gave the larger permeability increases with greater than 1,000 fold and 100 fold increases for the Lufkin and Houston Black clays, respectively.

While the initial permeability values obtained with water($0.01N\ CaSO_4$) were lower for the Lufkin clay, this clay usually ended up with the largest permeability values after treatment with the organic fluids. This may have been due to the larger shrink-swell capacity of the Lufkin clay.

Significant increases in permeability were obtained with basic, neutral-polar and neutral-nonpolar organic fluids over those values obtained with water. This indicates the need to test the permeability of clay liners with the actual leachates generated by a disposed waste especially where organic fluids may be present in the waste.

TABLE 2 PHYSICAL AND CHEMICAL PROPERTIES OF THE PERMEANTS TESTED

PERMEANTS Organic Fluids	Name	Water Solubility (gm/l) @ 20° C	Dielectric Constant @ 20°C	Dielectric Constant @ 25°C	Dipole Moment (debyes)	Temp. Range of the Liquid State (°C) Freezing	Temp. Range of the Liquid State (°C) Boiling	Viscosity (Centipoise) @ 20°C	Viscosity (Centipoise) @ 25°C	Density (g/cm³) @ 20°C	Molecular Weight
Acid, Carboxylic	Acetic Acid	∞	6.1		1.74	17	118	1.28	1.16	1.05	60
Base, Aromatic Amine	Aniline	34.0	6.9		1.55	-6	184	4.40	3.71	1.02	93
Neutral-Polar, Acetone	Acetone	∞		20.7	2.90	-95	56	0.33	0.32	0.79	58
Neutral-Polar, Glycol	Ethylene Glycol	∞	38.66		2.28	-13	198	21.0	17.3	1.11	62
Neutral-Non Polar Aliphatic	Heptane	0.003	1.0		0.00	-91	98	0.41	0.39	0.68	100
Neutral-Non Polar Aromatic	Xylene	0.20	2.5		0.40	-47	137	0.81	0.62	0.87	106
Water			80.4	78.5	1.83	0	100	1.0		.98	18

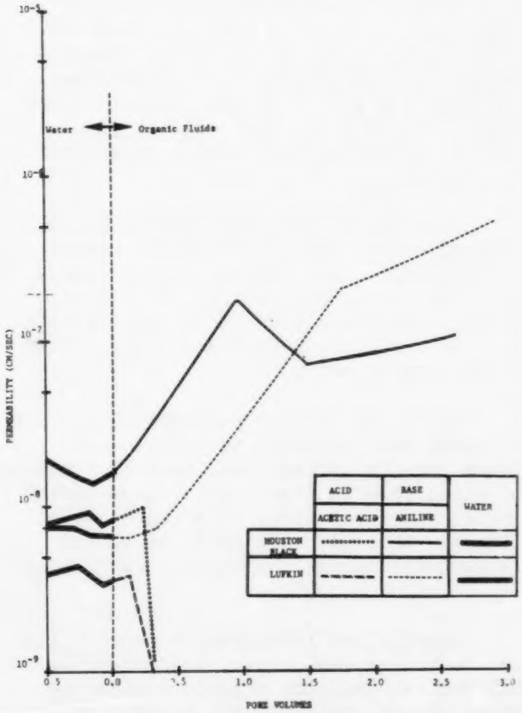


FIGURE 9. PERMEABILITY OF HOUSTON BLACK AND LUFKIN CLAY SOILS TO ACETIC ACID AND ANILINE.

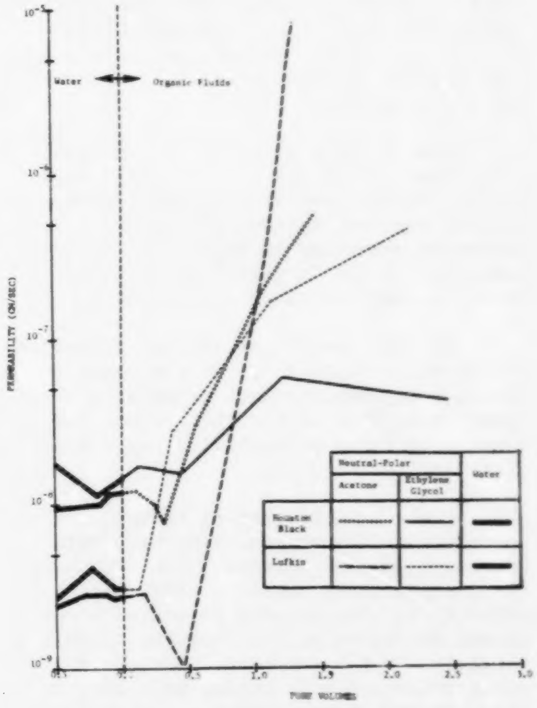


FIGURE 10. PERMEABILITY OF HOUSTON BLACK AND LUFKIN CLAY SOILS TO ACETONE AND ETHYLENE GLYCOL.

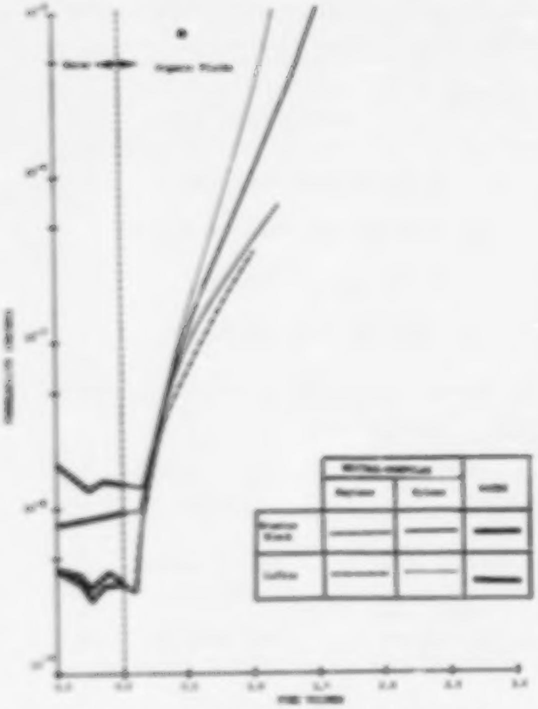


FIGURE 11. PERMEABILITY OF HOUSTON BLACK AND LUFKIN CLAY SOILS TO HEPTANE AND XYLENE.

CONCLUSIONS

An evaluation of the physical classes of hazardous waste indicated that many contain organic fluids. These fluids may in turn leach from the disposed waste and enter the clay liner. Permeability tests using two clay soils typical of those used to construct clay liners showed significant increases in permeability with several of the organic fluids studied. These results point to the need to test the permeability of clay liners with the actual leachates generated by the disposed wastes.

Ongoing tests are evaluating the effect organic fluids have on the permeability of kaolinitic and illitic clay soils. In addition, Phase II tests are planned for evaluating the effects of organic and aqueous based fluid mixtures and waste leachates on the permeability of kaolinitic, illitic, and commercially prepared clay liner products (Table 3).

REFERENCES

1. Bennett, J. P. 1966. "Permeability of soils at elevated permeant pressures." Masters Thesis at Colorado State University, Fort Collins, Colorado.

2. Bowles, J.E. 1968."Coefficient of permeability-Falling Head Method" pp. 105-110. In Eng. Prop. of Soils and their Measurement. McGraw Hill Book Co., N.Y., N.Y.

3. Brown, K. W. and David Anderson. 1980. "Effect of organic chemicals on clay liner permeability." In: Proceedings of 6th Annual Research Symposium. EPA-600/9-80-010. U.S. Environmental Protection Agency, Cincinnati, Ohio. pp. 123-134. PB 80-175086.

4. Cheremisonoff, N. P., P. N. Cheremisonoff, F. Ellerbusch, and A. J. Perna. 1979. Industrial and Hazardous Wastes Impoundments. Ann Arbor Sci. Publ. Inc., Ann Arbor, Michigan.

5. Christiansen, J. E., M. Fireman, and L. E. Allison. 1946. "Displacement of Soil-Air by CO_2 for Permeability Tests." Soil Science. Vol. 61 pp. 355-365.

6. EPA. 1974. Report to Congress: Disposal of Hazardous Waste. USEPA #SW 115. Washington, D.C.

7. Goring, C.A.I. and John W. Hamaker. 1972. Organic Chemicals in the Soil Environment, Vol. I & II. Marcel Dekker, Inc., N.Y., N.Y.

8. Jones, C. W. 1960. "Permeability tests with the permeant water under pressure". Earth Laboratory Report #EM-559. Division of Engineering Laboratories, Commissioner's Office, Denver, Colorado.

9. Sherard, J. L. and R. S. Decker. 1977. "Summary-evaluation of the symposium on dispersive clays." Dispersive Clays, Related Piping and Erosion in Geotechnical Projects. ASTM STP 623. J. L. Sherard and R. S. Decker (eds.).

TABLE 3. FLUIDS AND CLAY LINERS TO BE EVALUATED IN THE PHASE II LABORATORY STUDY

CLAY LINERS

COMMERCIALLY PREPARED	NATIVE CLAY SOILS
1. Sodium Saturated Smectite	1. Mixed Cation Smectite
2. Organic Polymer Treated Smectite	2. Calcium Saturated Smectite
	3. Mixed Cation Illite
	4. Mixed Cation Kaolinite

FLUIDS

ORGANIC BASED MIXTURES	AQUEOUS BASED MIXTURES	LIQUID INDUSTRIAL WASTES
Various mixtures of the organic fluids used in Phase I (eg. 50% xylene in acetone, etc.)	Various mixtures of miscible organic fluids in a water base (eg. 10:10:80 acetone: ethylene glycol:water, etc.).	1. Spent solvent wastes 2. Off specification liquid products

MEMBRANE LINER SYSTEMS FOR HAZARDOUS WASTE LANDFILLS

Robert C. Gunkel
U. S. Army Engineer Waterways Experiment Station
Vicksburg, Mississippi 39180

ABSTRACT

A series of tests were conducted to determine an economical method of protecting flexible membranes from damage during the construction of landfills. Subgrade soils were selected that were considered to be representative of those which would be found in areas where landfills are constructed. Four membranes were tested. The membranes were placed on top of the subgrades and covered with various thicknesses of a sand material. The test items were trafficked using three different vehicles that were representative of the type of loadings that could be applied during landfill construction. Performance of the membranes was judged by their resistance to puncture and wear.

Introduction

Background

Today, many industrial wastes may be highly toxic to the environment if their disposal is not properly controlled. A common method for disposal is the use of landfills, but improperly designed landfills could result in contamination of ground and surface water by toxic waste material. This condition exists because of various physical, chemical, and biological processes occurring when water or fluids percolate through the wastes, resulting in a leachate which contaminates the soil and ground water. The placement of impervious flexible membrane over the subgrade material in hazardous waste landfills could be one solution to controlling the leachate. One problem associated with this approach is potential damage to the membrane caused by earthmoving equipment during construction. Not only does the heavy equipment tend to damage the liner material, but puncture of the flexible membrane by underlying angular rock and soil particles in the natural soil also presents a source of damage. To study the problem, the Environmental Protection Agency (EPA) requested the U. S. Army Engineer Waterways Experiment Station (WES) to conduct an investigation to determine the requirements needed to protect flexible membrane from damage.

Objective

The objective of this study was to determine an economical method to protect flexible membranes from damage during the construction of landfills.

Scope

The performance of flexible membranes used as liners in landfills was investigated. A test section containing 12 test items was constructed and subjected to three types of vehicle traffic (tracked, pneumatic-tired, and cleated). During this study four flexible membranes, six selected subgrades, three thicknesses of a sand protective layer, and bedding materials were investigated. The materials used, the construction of the test section, the tests that were conducted, and the results including some conclusions and recommendations are described below.

Construction and Materials

Construction

A test section was constructed under shelter at the WES. The test section was 16 ft wide, 240 ft long, and consisted of 12 test items, each 20 ft long and 16 ft wide. A plan and profile of the test section are shown in Figures 1 and 2, respectively. Construction was started by

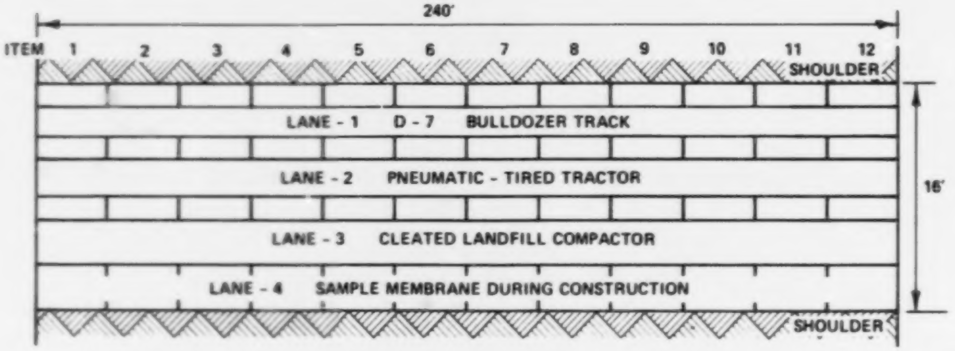

240'
ITEM 1 2 3 4 5 6 7 8 9 10 11 12
SHOULDER
LANE - 1 D - 7 BULLDOZER TRACK
LANE - 2 PNEUMATIC - TIRED TRACTOR
LANE - 3 CLEATED LANDFILL COMPACTOR
LANE - 4 SAMPLE MEMBRANE DURING CONSTRUCTION
16'
SHOULDER

Figure 1. Plan view of test section

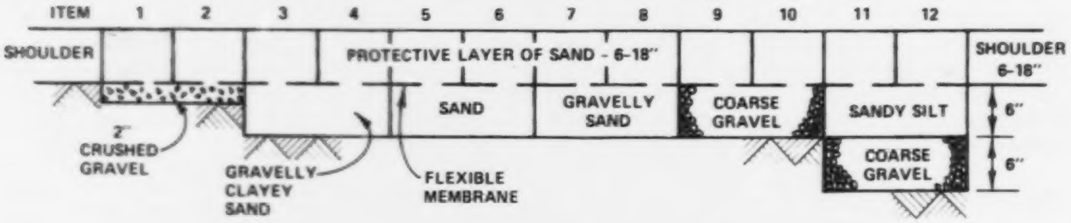

ITEM 1 2 3 4 5 6 7 8 9 10 11 12
SHOULDER
PROTECTIVE LAYER OF SAND - 6-18"
SHOULDER 6-18"
SAND
GRAVELLY SAND
COARSE GRAVEL
SANDY SILT
6"
COARSE GRAVEL
6"
2" CRUSHED GRAVEL
GRAVELLY CLAYEY SAND
FLEXIBLE MEMBRANE

Figure 2. Profile of test section

excavating an area of the subgrade floor of the shelter, where the test section had been staked out, to a depth of 6 in. and a width of 16 ft (Figure 3). The last 40 ft, at the north end of the test section, was excavated to a depth of 12 in. to accommodate a 6-in. layer of coarse gravel that was overlaid with 6 in. of sandy silt. This fine grained sandy silt was used to act as a bedding material to protect the flexible membranes from puncture during traffic tests. The remainder of the test section was backfilled with the selected subgrades. The subgrades were compacted with pneumatic-tired and vibratory rollers. Figure 4 shows the test section with the selected subgrades in place. After the six subgrades had been placed, each of the 12 test items in the test section was covered with flexible membranes. Shoulders were constructed on both sides of the test sections using material that had been excavated previously from the shelter floor. The height of the shoulders depended on the thickness of the protective layers of sand that were placed over the membrane liners for each test program. For the first program, the shoulders were 6 in. in height so as to contain that depth of sand. The sand was dumped between the shoulders at each end of the test section. Then a bulldozer pushed the sand toward the center of the test section. Care was taken during placement operations to maintain at least 6 in. of sand between the dozer's tracks and the flexible membranes. Figure 5 shows the completed test section with a protective sand layer of 6 in.

Figure 3. Test section prior to placement of selected subgrades

Figure 4. Overall view of test section with subgrades in place

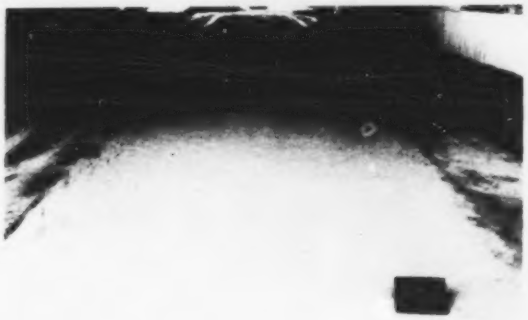


Figure 5. Completed test section with 6 in. of protective sand

Subgrade Material

Six subgrade materials were selected and used for the 12 items of the test section. These materials were classified according to the Unified Soil Classification System (USCS) as follows:

Item No.	Classification
1-2	Crushed gravel (GP)
3-4	Gravelly clayey sand (SP-SC)
5-6	Sand (SP)
7-8	Gravelly sand (SP)
9-10	Coarse gravel (GP)
11-12	Sandy silt (ML)

It should be noted that the sand in items 5 and 6 was the same type of sand that was used for the protective layers. The sand was a local (Vicksburg, Mississippi) sand usually used normally as the fine aggregate in concrete.

Membranes

The four flexible membranes and one fabric used as a bedding material were as follows:

Designation*	Thickness mils	Type
M-1	20	Elasticized polyolefin (3110)
M-2	20	Polyvinyl chloride (PVC)
M-3	30	Chlorinated polyethylene (CPE)
M-4	36	Reinforced chlorosulfated polyethylene (CSPE)
F-1	30	Nonwoven polypropylene and nylon

---

* The membranes and fabric material are referred to hereafter by the designation symbol assigned above.

Traffic Vehicles

The vehicles used to apply traffic to the various test programs were: A D-7 bulldozer equipped with 22-in.-wide tracks, weighing approximately 44,000 lb, and having a contact pressure of 9 psi; a pneumatic-tired tractor weighing 37,190 lb and equipped with two 29.5x29, 22-ply tires (each tire had a contact area of 574 sq in. which produced a contact pressure of 32 psi); and a model 816 landfill compactor weighing 40,900 lb equipped with four cleated steel wheels having a contact pressure of 18 psi. The traffic vehicles are shown in Figures 6-8.

Tests, Data Collection, and Failure Criteria

Traffic Pattern

Traffic tests were conducted on each test item to simulate actual heavy equipment operations during the construction of landfills. Traffic was applied with both the "tracted dozer" and "cleated landfill compactor" in the same manner. These vehicles were operated in one direction

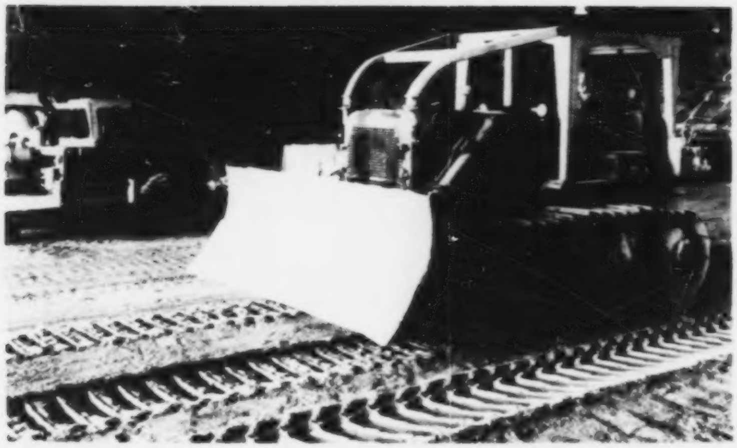


Figure 6. D-7 bulldozer

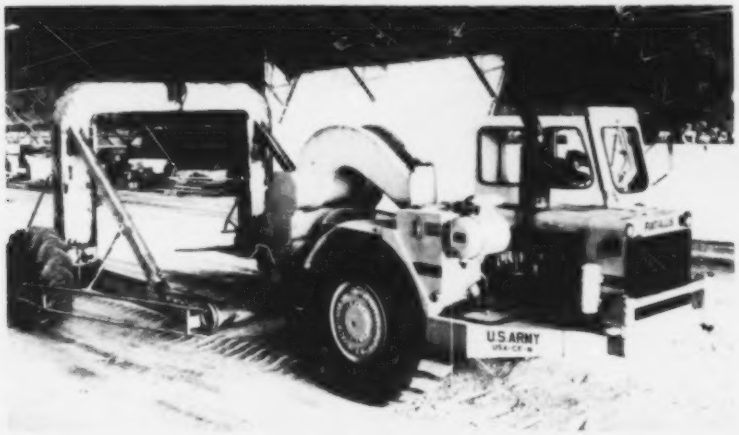


Figure 7. Pneumatic-tired tractor

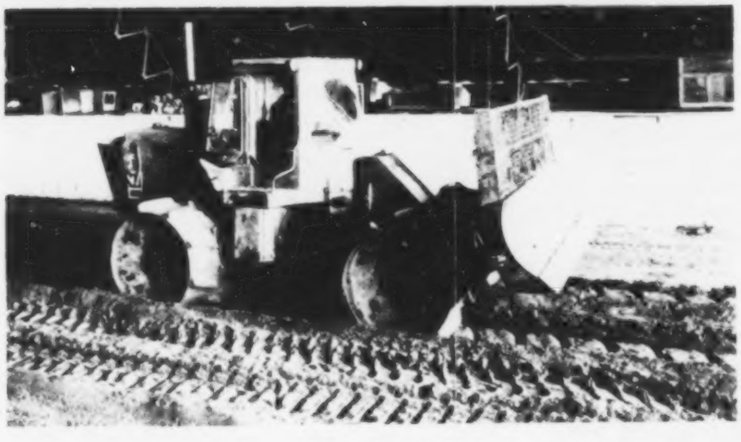


Figure 8. Cleated landfill compactor

until they had traveled the entire length of the section where they were stopped and then returned in the same track or wheel path in reverse. The pneumatic-tired tractor was operated in the same direction and in the same wheel path as it had traveled in the preceding pass. One pass of the dozer and pneumatic-tired tractor resulted in one coverage within their respective traffic lanes while one pass of the landfill compactor resulted in two coverages within the traffic lane.

Soil Data

Except for the crushed and coarse gravel material, laboratory compaction tests and unsoaked CBR's were performed on the selected subgrades. Field tests to determine moisture content, density, and CBR value on the in-place material of the test section were also performed. The results of the soil data obtained from these tests are presented in Table 1.

Membrane Evaluation

In evaluating flexible membrane performance, only the after-traffic condition was considered. After 10 passes of the traffic vehicles, a trench was excavated across each traffic lane in all 12 items. A sample of the membrane was removed from each lane in each item, marked for identification, and inspected. After patching the membrane and replacing the protective layer of sand in the trenches, traffic was continued on the items in which the membranes showed only a few or no punctures. After 30 passes, traffic was stopped and a final inspection was made.

Failure Criteria

Each sample of membrane was placed over a light table and inspected for punctures. A 5-sq-ft area, within the wheel path, was marked on the membranes and the number of punctures in this area was recorded. A membrane was considered "failed" if any punctures were noted.

Traffic Testing

Test Program 1

In test program 1, two types of membranes (M-1 and M-2) were placed over the six subgrade materials. The M-1 and M-2 membranes were placed on the odd- and even-numbered items, respectively. A 6-in.-thick sand cover was placed over the membranes to act as a protective layer. Traffic was applied to the test section with the D-7 tracked bulldozer and the pneumatic-tired tractor. After 10 passes, traffic was stopped and trenches were dug across the traffic lanes in each of the 10 items. Samples of the membrane from each traffic lane and each item were removed for inspection. Figures 9 and 10 show a typical inspection trench and the condition of the membrane sample after removal. After patching the void in the membrane and replacing the protective layer of sand in the trenches, traffic was continued on items 5-6 and 11-12 which showed only a few or no punctures in the membranes. After 30 passes were completed, traffic was again stopped and a final inspection was made. The final results for test program 1 are graphically displayed in Figure 11.

TABLE 1. SOILS DATA

		Field tests			Laboratory tests		
Item No.	Soil classification	Dry density pcf	Moisture content	CBR	Max density* pcf	Optimum moisture	Unsoaked CBR
3-4	Gravelly clayey sand	125.8	9.8	7.0	131.8	7.4	20.4
5-6	Sand	104.1	8.1	4.0	105.6	14.0	30.5
7-8	Gravelly sand	118.6	6.0	8.3	126.6	8.0	21.3
11-12	Sandy silt	98.5	18.7	7.0	105.5	14.8	24.4

* CE-12 compactive effort.

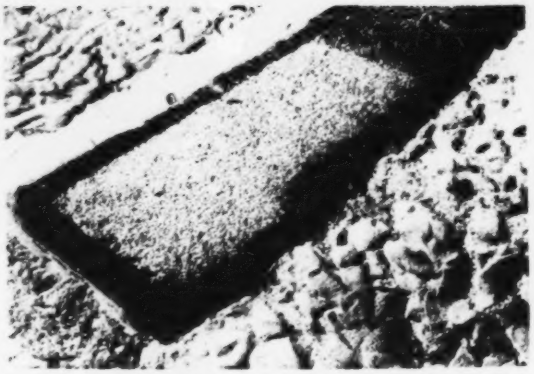


Figure 9. Typical view of inspection after removal of membrane

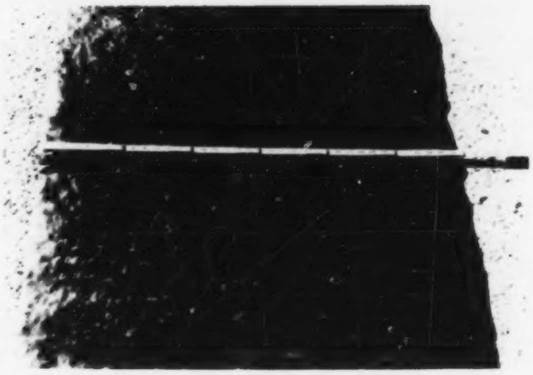


Figure 10. View of holes in membrane after 10 passes of the pneumatic-tired tractor

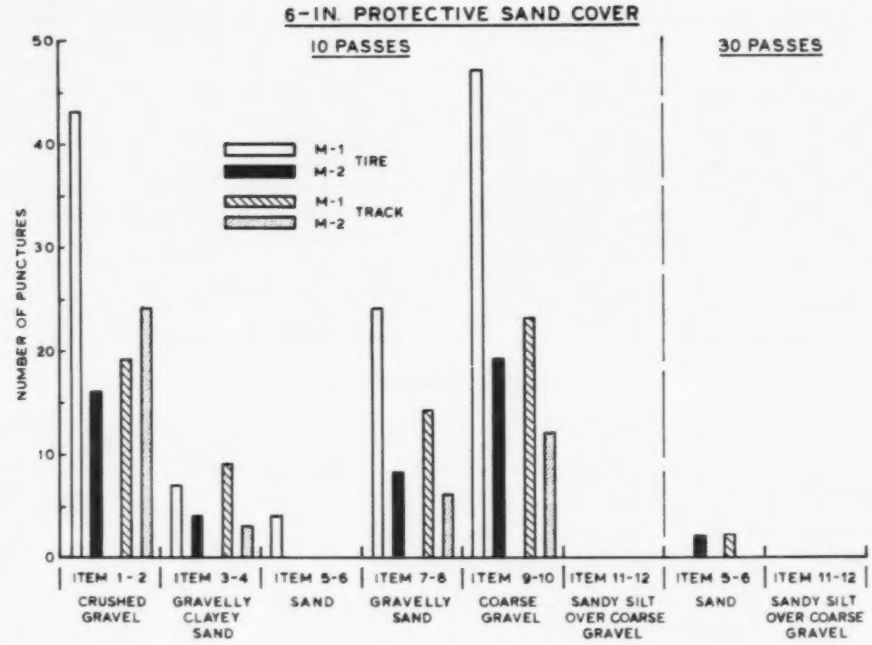


Figure 11. Results of test program 1

Test Program 2

Test program 2 was identical to the first test program with the exception of the thickness of the sand protective layer which was increased from 6 to 18 in. In trafficking test program 2, three types of vehicles were used (track-tire-cleated). The cleated vehicle was a "Model 816 Landfill Compactor" which was owned by Bolivar County, Mississippi, and was operated at one of their landfill sites. The 816 landfill compactor was leased for testing of test program 2. After traffic, the sampling of the membrane was accomplished in the same manner as in test program 1. Typical rutting that occurred in the sand protective layer during traffic operations is shown in Figure 12. Final results of test program 2 are shown in Figure 13.

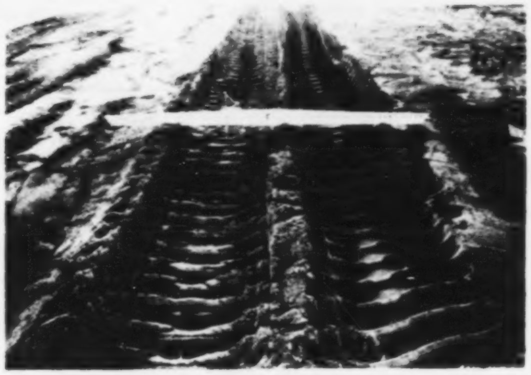


Figure 12. Lane 1 (track), lane 2 (tire) rutting after 30 passes

Test Program 3

After trafficking and obtaining the final data in test program 2, the sand protective layer and membranes were removed and preparation of test program 3 was started. Test program 3 contained the same selected subgrades, and 18 in. of sand was placed as the protective layer. However, the existing 20-ft-long items were subdivided into two 10-ft-long subitems which resulted in four separate test items in each of the six types of subgrade materials. The four test subitems per subgrade material were overlaid with membranes M-1, M-2, M-3, and M-4, respectively. A nonwoven fabric material (F-1), used as a separation barrier or a bedding material, was placed between the M-1 and M-2 membranes and the subgrade. Test results for test program 3 after trafficking with the D-7 bulldozer and the pneumatic-tired tractor are presented in Figure 14.

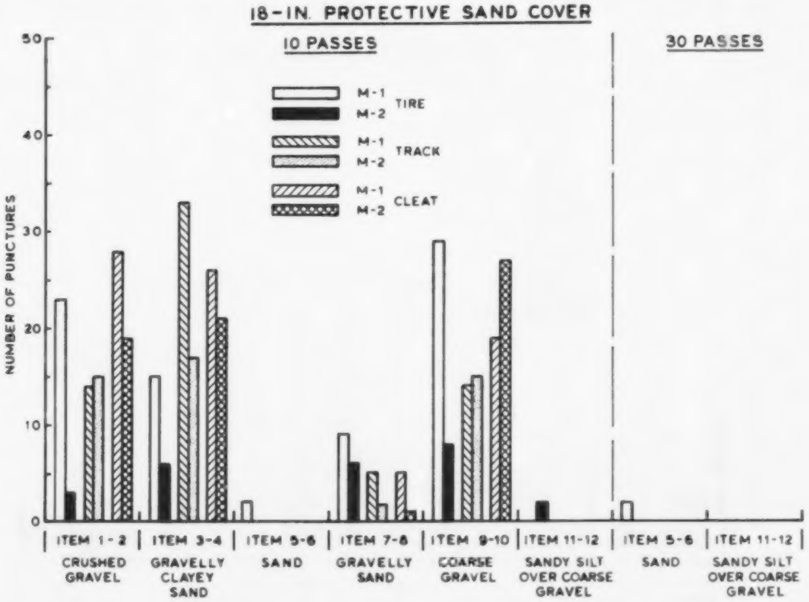


Figure 13. Results of test program 2

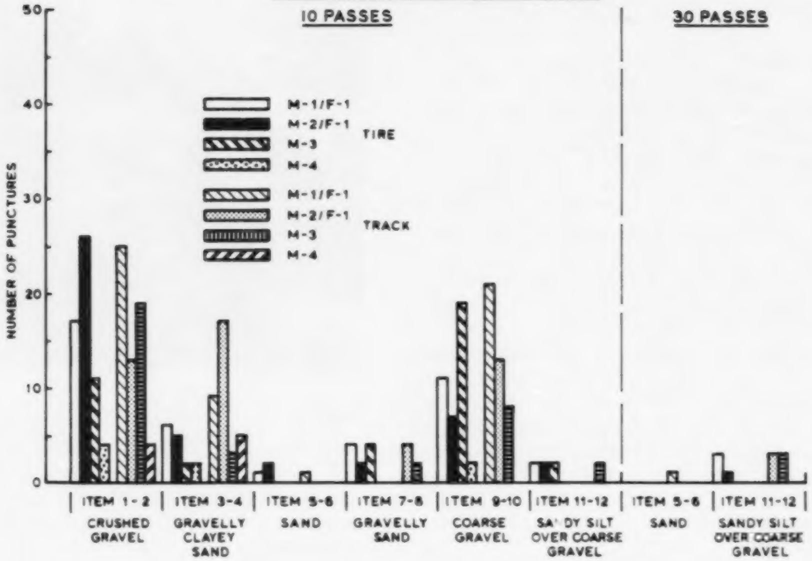


Figure 14. Results of test program 3

Test Program 4

After completion of test program 3, 6 in. of the protective sand layer and 6 in. of the shoulders were removed from the entire test section. With the protective layer of sand now 12 in. in thickness, another series of traffic tests was performed using the same two vehicles. During this test program, traffic was applied to the various test items by moving the test vehicles to lanes 3 and 4 of the test section. Results from this series of tests are shown in Figure 15.

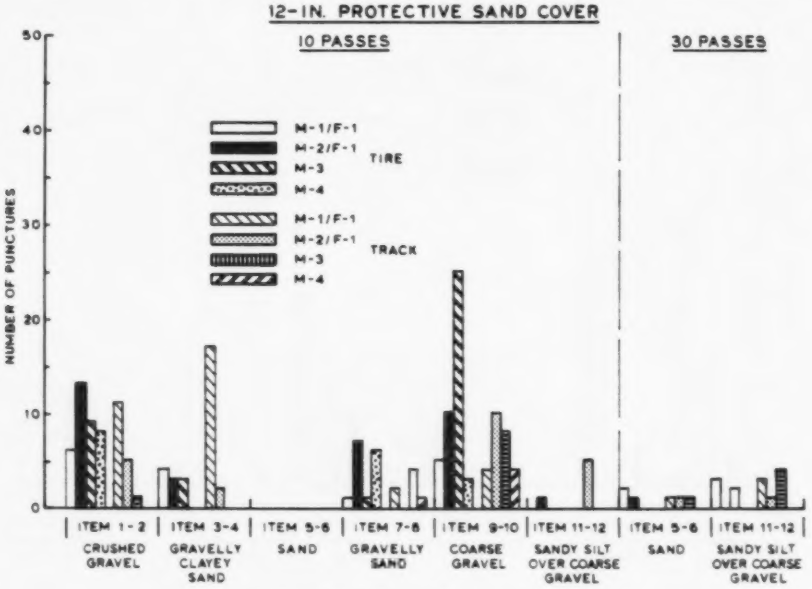


Figure 15. Results of test program 4

Discussion of Results

The large number of punctures that were noted in the four flexible membranes tested was attributed to the selected subgrades used in the construction of the test section. Five of the six subgrades contained large percentages of sand and gravel with only a small amount of fines. The one remaining soil that was used in the test section was classified as a sandy silt. This fine-grained sandy silt soil was used as a bedding material, and 6 in. of it were placed over the coarse gravel in items 11 and 12. The purpose of the bedding was to act as a protection barrier between the coarse gravel and the flexible membrane. For comparison purposes, items 9 and 10 contained the same coarse gravel subgrade but were not covered with the sandy silt bedding material. Final results were quite evident that the bedding material used in items 11 and 12 aided in the protection of the flexible membrane by reducing the number of punctures. During test programs 3 and 4, another type of bedding material was used. A nonwoven polypropylene and nylon-type material (F-1) was placed under membranes M-1 and M-2 during traffic testing. After final inspection of the membranes and a comparison of results from test program 2, no significant reduction in the number of punctures was noted.

It was also observed during the inspection of the trafficked membrane that most of the punctures detected occurred form the bottom in an upward direction. Because of these observations, it is assumed that subgrades containing angular gravel and coarse soil particles require a bedding and/or cushioning material to prevent punctures.

The four membranes investigated during this study received numerous punctures when subjected to the subgrades containing gravel-size material. However, a considerable decrease in the number of punctures was observed when the membranes were trafficked on the items containing the sand and sandy silt subgrades. After completion of some traffic operations on these test items, no punctures were detected in several of the membranes.

It was also observed that the three types of vehicle loadings (track, tire, and cleated) used to apply traffic to the membranes produced similar amounts of damage.

Conclusions

Based on the results of the traffic tests performed and the observations made during the inspection of the flexible membranes, the following conclusions are presented:

The three traffic vehicles produced similar amounts of damage to each membrane.

All membranes showed less damage when trafficked on the sand and sandy silt subgrades than on the subgrades containing gravel.

The 6 in. of bedding material placed in items 11 and 12 reduced the number of punctures in the membranes.

From information obtained from this study, it was assumed that both a bedding and protective cover will be necessary to protect a flexible membrane from puncture during the construction of landfills.

The fabric material, used as a bedding, did not perform satisfactorily as it permitted punctures to the liners.

Because of the limited data, thickness requirements for the bedding and protective soil layer could not be determined.

DURABILITY OF LINER MATERIALS FOR HAZARDOUS WASTE DISPOSAL FACILITIES

H. E. Haxo, Jr.
Matrecon, Inc.
Oakland, California 94623

ABSTRACT

The results of several exposures of a variety of samples of soil, admix, sprayed-on, and polymeric membrane liners to a selected group of real hazardous wastes and three test fluids, i.e. distilled water, 5% aqueous solution of sodium chloride, and a saturated solution of tributyl phosphate are discussed. The exposures included the primary test of 12 liners in contact with 6 wastes for three years, immersion tests of 12 polymeric membranes in 9 wastes for up to 2.25 years, and roof exposure of polymeric membranes and wastes. Most of these results have been reported at previous research symposia and in interim reports.

The effects of the exposures vary greatly with liner materials and with wastes. The effect of minor amounts of organic constituents in a waste can have significant effects on liner materials on prolonged exposure. The degree of swelling of polymeric membranes in contact with a waste is a measure of the compatibility of the liner with the waste. The greater the swelling the less the compatibility. Swelling of a membrane results in the loss of physical properties such as tensile strength, elongation at break, and tear strength. Major factors in the swelling of a membrane in a given waste are its solubility parameter with respect to that of the waste, its degree of crosslinking and crystallinity, and the presence of water soluble constituents in the membrane compound.

No single liner material in the test program appears to satisfy all of the requirements for all wastes. The complexity of the various waste streams requires that compatibility tests must be run to demonstrate the durability of the lining material under consideration with the waste which is to be impounded. Liners based on polymers with crystallinity appear to be more resistant to water and chemicals than the other polymeric materials.

INTRODUCTION

This research study of liners was started in 1975 with the primary purpose of assessing interaction of a broad range of lining materials and a selected, representative series of hazardous wastes. The linings considered for this project included all major types of man-made linings, i.e., compacted native soils and clays, admixed liner materials, spray-on membranes, and flexible polymeric membrane materials.

The primary thrust of the project was to expose two specimens each of one compacted native soil, three admixes, one sprayed-on membrane, and eight polymeric membranes to wastes under conditions which simulated those that might be encountered in actual service. The specimens were of sufficient size so that, when they were recovered from the exposure cells, tests could be made of some of their physical properties. One square foot surface of each material was exposed under one foot of depth to the selected wastes.

In addition, supplemental work was done to measure overall characteristics of lining materials and to develop test methods which might be used in the selection of specific materials for a given waste disposal facility. Interim data have been presented at three previous annual research symposia (Haxo, 1976; Haxo, 1978; Haxo, 1980a) and one interim report has been published (Haxo et al., 1977). At the Sixth Annual Conference in March of 1980, the results of three years of exposure to the wastes were reported. These results and those relating to liners for MSW landfills are discussed in the Technical Resource Document, "Lining of Waste Impoundment and Disposal Facilities" (Matrecon, Inc.), which EPA made available for public review in December 1980.

Though new data have been obtained and are presented, the principal objective of this paper is to discuss the results that have been obtained with particular reference to the durability of lining materials that have been exposed to the various wastes on pilot, bench, and laboratory scales which simulate service conditions.

LINING MATERIALS

The purpose of lining a waste disposal site is to prevent the potentially polluting constituents of the waste from leaving the site and entering the groundwater or surface water system in the proximity of the site. The pollutants include organic and inorganic materials, solids, liquids, gases, and bacteriological species. In their performance liners function by two mechanisms:

a. To impede the flow (flux) of the pollutant and pollutant carrier, usually water, into the subsoil and thence into the groundwater. This requires a construction material having low permeability.

b. To absorb or attenuate suspended or dissolved pollutants, whether organic or inorganic, in order to reduce the concentrations so that they fall within the ranges set by the EPA for groundwater. This absorptive or attenuative capability is dependent largely upon the chemical composition of the liner material and its mass.

Most liner materials function by both mechanisms but to different degrees depending on the type of liner material and the waste fluid and constituents. Polymeric membrane liners are the most impermeable of the liner materials, but have little capacity to absorb materials from the waste. They can absorb a relatively small amount of organic material but, due to their small mass, their total absorption is small. Soils can have a large capacity to absorb materials of different types, but they are considerably more permeable than a polymeric membrane. However, the greater thickness of the soil can result in low flux through the liner. The choice of a particular liner material for a given site will depend upon many factors.

We consider a liner to be a material constructed or fabricated by man. Such a definition includes soils and clays having low permeability which are either brought to a site or available on the site and compacted or remolded to reduce permeability and increase strength.

Liners can be classified in a variety of ways, such as by construction method, physical properties, permeability, composition, or type of service. Some of these classifications are presented in more detail in Table 1. In this project, the types of liners that were studied are:

- Admixes
- Soils and clays
- Sprayed-on membranes
- Polymeric membrane liners

These materials had been used in water containment and conveyance and appeared to be promising for use in the impoundment of hazardous wastes.

The specific types of materials, with their respective thicknesses, selected for the exposure testing are:

Admixes:

Hydraulic asphalt concrete (2.5 in.)

Modified bentonite and sand (5.0 in.)

Soil cement, with and without surface seal (4.0 in.)

Soil:

Compacted native fine-grain soil (12.0 in.)

TABLE 1. CLASSIFICATION OF LINERS FOR WASTE DISPOSAL FACILITIES

A. BY CONSTRUCTION:

- Onsite construction:
  - Raw materials brought to site and liner constructed on site.
  - Compacted soil.
  - Mixed on site or brought to site mixed.
  - Sprayed-on liner.
- Prefabricated:
  - Drop-in polymeric membrane liner.
- Partially prefabricated:
  - Panels brought to site and assembled on prepared site.

B. BY STRUCTURE:

- Rigid (some with structural strength)
  - Soil
  - Soil cement
- Semirigid
  - Asphalt concrete
- Flexible (no structural strength)
  - Polymeric membranes
  - Sprayed-on membranes

C. BY MATERIALS AND METHOD OF APPLICATION:

- Compacted soils and clays.
- Admixes, e.g. asphalt concrete, soil cement.
- Polymeric membranes, e.g. rubber and plastic sheetings.
- Sprayed-on membrane linings.
- Soil sealants.
- Chemisorptive liners.

Sprayed-on:

- Emulsified asphalt on a nonwoven fabric (0.3 in.)

Polymeric membranes:

- Butyl rubber, fabric reinforced (34 mils)
- Chlorinated polyethylene (32 mils)
- Chlorosulfonated polyethylene, fabric reinforced (34 mils)
- Elasticized polyolefin (20 mils)
- Ethylene propylene rubber (50 mils)
- Neoprene, fabric reinforced (32 mils)
- Polyester elastomer, experimental (8 mils)
- Polyvinyl chloride (30 mils).

EXPOSURE CONDITIONS OF LINERS IN SERVICE IN HAZARDOUS WASTE IMPOUNDMENTS

Field Service Conditions

To estimate the durability or the service life of a product, the environmental conditions in which it serves must be known and understood. The service conditions encountered by a liner for a hazardous waste impoundment contrast greatly with those encountered by a liner in a landfill. In the latter case, the usual environment of a liner is anaerobic, cool, dark, and continually moist (Haxo, 1976). Also, the waste fluid or leachate, though variable from landfill to landfill and even within a landfill, will not be as variable or as highly concentrated in pollutants or in constituents that are aggressive to liner materials as is encountered in a waste disposal facility that contains industrial, hazardous, and toxic wastes.

Some of the conditions that could be encountered by liners in hazardous waste impoundments are:

- Exposure to a vast array of different materials in direct contact or under soil cover.
- Exposure to weather, e.g. sunlight, rain, wind, ozone, and heat.
- Wave action of the fluid in the pond.
- Intermittent exposure to both waste fluids and weather.
- Low and high temperatures.
- Burrowing and hoofed animals.
- Ground movement.
- Irregularity of the soil beneath a liner.
- Changing temperatures.

These conditions must be recognized in evaluating materials in the laboratory or on a pilot scale.

Simulating Test Conditions

In conducting this research, our basic approach was to expose specimens of various commercial lining materials under conditions which simulated real service, to use actual wastes, to measure seepage through the specimens, and to measure effects of exposure by following changes in important physical properties of the respective lining materials.

All lining materials were subjected to two types of exposure testing:

- Bench screening tests in which small specimens were immersed in wastes.
- One-side exposure to wastes in primary exposure cells.

In addition to these two types of tests, selected polymeric membranes were subjected to the following additional tests which simulate different aspects of actual field service:

- Immersion in wastes.
- Roof exposure on rack.
- Outdoor exposure of small membrane lined tubs containing wastes.
- Water absorption.
- Membrane pouches containing wastes, placed in deionized water.

Bench Scale Screening Test

All of the different types of liner materials were subjected to a screening test to select materials for the long-term testing. Strips of the membranes were immersed in the waste fluids and those materials that swelled inordinately in a matter of a few weeks were eliminated from further consideration with that particular waste. In the case of the admix liners, small cylindrical specimens were sealed in short sections of glass pipes and covered with six inches of waste. If the liner leaked in a short time, i.e. about one month, it was eliminated from testing with that particular waste.

Exposure of Primary Liner Specimens

The exposure cells for the primary specimens are shown schematically in Figures 1 and 2. Figure 1 shows the cell for the thick admix and soil liners and Figure 2 shows the cell for the membrane specimens. Each membrane specimen was prepared with a field-type seam across the center made according to the recommended practice of the respective supplier of the membrane. Two specimens of each liner material were placed in separate cells which were loaded with portions of the same waste. Two sets of cells were placed in exposure. Cells were dismantled at two times and the specimens were recovered, analyzed, and their physical properties measured.

Immersion Tests

Concurrent with the exposure of the primary liners in the bases of the cells,

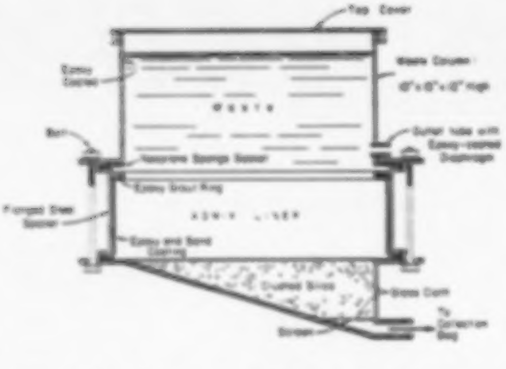

Top Cover
Epoxy Coated
Waste Column
Waste
Bolt
Outlet tube with Epoxy-coated Diaphragm
Neoprene Sponge Gasket
Epoxy Grout Ring
Flanged Steel Spacer
Admix Liner
Epoxy and Sand Coating
Crushed Stone
Glass Cloth
Screen
To Collection Bag

Figure 1. Exposure cell for thick liners.

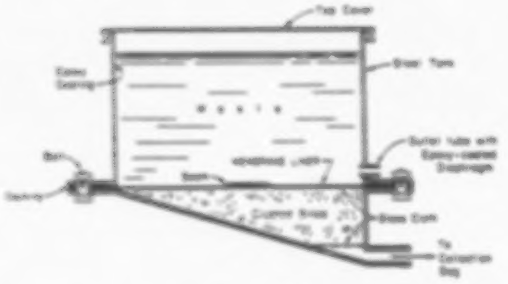

Top Cover
Steel Tank
Epoxy Coating
Waste
Outlet tube with Epoxy-coated Diaphragm
Bolt
Membrane Liner
Seam
Crushed Stone
Glass Cloth
To Collection Bag

Figure 2. Exposure cells for membrane liners. Dimensions of the steel tank are 10 x 15 x 13 inches in width, length, and height.

supplemental polymeric membrane liner specimens were hung in the wastes. The effects of exposure were measured by determining the increase in weight, analyzing the exposed specimens, and measuring selected physical properties. Details of the procedure followed in conducting the immersion tests are presented in the Manual (Matrecon, Inc., 1980). Detailed results of the test have been reported (Haxo, 1978; Haxo, 1980a; Haxo, 1981b; Matrecon, Inc., 1980).

Roof Exposure of Specimens Mounted on Rack

These specimens were six-inch squares cut from the polymeric sheetings and mounted at 45° on a rack facing southward on the roof of our laboratory in Oakland, California. On removal from the rack, the samples were cleaned, weighed, and their dimensions measured, after which selected physical properties were measured.

Such a test can only be comparative of the specimens under test. Each test location is different. No mechanical stress is applied to the specimens, which lie on a flat surface. The specimens are exposed in a static condition to ultraviolet and heat from sunlight, and to wind and rain.

Roof Exposure of Liners in Tubs Filled with Wastes

In addition to the small slabs of liners which were exposed to the weather on the roof rack, 12 small tubs were lined with various polymeric membranes and filled with wastes. In this test, which is continuing, nine different lining materials were exposed to four different wastes. Each test specimen was greater than one square yard, had a field seam through the middle, and many folds of different severity.

This type of test simulates exposed liners in open ponds. The liner contacts the waste at various depths. Thus, if the waste is multi-layered, the liner will contact all layers. Also, the liner simultaneously contacts the air as well as the waste. A zone of the liner is intermittently exposed to air, then waste, etc. Another variable in this test is the direction faced by the sheeting; the exposure to sunlight and wind varies for the different sides of the tub.

Water Absorption

As most wastes contain water which most polymeric materials absorb to varying degrees, the water absorption of a series of liners is being measured for extended periods of time in accordance with ASTM D570. In this test, small, 1 x 3 inch specimens are immersed in water. In addition to water absorption, the loss of soluble fraction can be assessed at the end of the exposure. The test specimens are too small to test properties; generally, one tensile measurement can be made.

Pouch Test

In this test, small pouches are fabricated of the membranes to be tested and are filled with wastes or other test fluids, such as salt water, sealed, and immersed in deionized water. The permeabilities of the membranes to water and to pollutants are determined by observing, respectively, the change in weights of the bags and the measurements of pH and electrical conductivity of the deionized water. Due to osmosis, water should enter the pouch, and ions and dissolved constituents should leave the bag. Details of the test procedure are presented in the Technical Resource Document (Matrecon, Inc., 1980). A schematic representation of the pouch test showing the movement of the various constituents in shown in Figure 3.

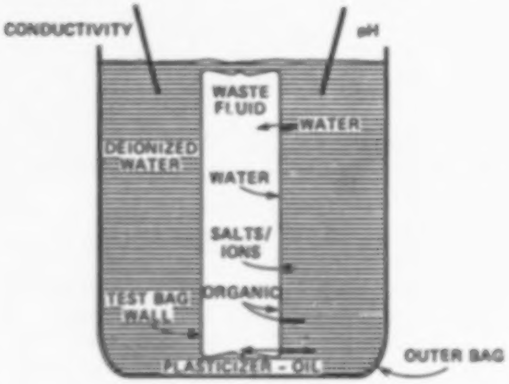


Figure 3. Schematic representation of the movements of the mobile constituents in the pouch test of membrane liner materials.

The initial tests were made with thermoplastic materials because they could be fabricated into pouches with relative ease by heat sealing. Some of these pouches have now been exposed more than 1000 days.

Bags containing the wastes actually increased in weight, indicating the flow of water into the bags through osmosis. The long-term tests now show that some ionic material is diffusing through the liners into the deionized water.

WASTES AND WASTE FLUIDS

Not only do the waste fluids contain pollutants which could contaminate groundwater, but these fluids can also contain agents that are aggressive to various liners. The principal constituent of most wastes is water, which in itself can be an aggressive agent to many materials. In addition, waste fluids generally contain dissolved organic and inorganic components that can cause deterioration depending upon the type of liner and the amount and type of the agent. Organic constituents are particularly aggressive to most of the liners that are considered for lining waste impoundments. Even in minor amounts in the fluid, these organic constituents can swell or dissolve the organic types of lining materials. Furthermore, these agents can affect some soils. The dissolved salts, although not generally aggressive toward the membrane-type liners, can be aggressive toward some soils. Strong acids and strong bases can affect most lining materials. The composition of the waste fluids that were used in this study are presented Table 2.

After the primary exposure tests, specimens of these wastes were collected and are being re-analyzed to determine the effects of change in composition during exposure periods. Some of the liner specimens were sufficiently massive, e.g. the soil, that they might have absorbed components from the fluid above them and thus reduced the concentration of pollutants and aggressive agents within the waste fluids. Another factor relating to the waste fluid that was apparent in the work was the inhomogeneity of some of the wastes. Several of the wastes were single-component solutions; others were mixtures of oils and water, each with dissolved constituents. Consequently, in several cases the wastes that were in the cells were in two layers with the oily components on the top. This inhomogeneity resulted in different effects upon the liners, depending upon the depth at which the liner was tested.

In addition, to the real wastes that were used in the exposure tests, we added three additional tests fluids, i.e. distilled water, a 5% solution of Na Cl in water, and a saturated solution of tributyl phosphate in water. Distilled water and brine solutions are commonly used as test fluids for assessing rubber and plastic materials. In many situations, the distilled water causes more swelling and loss of properties than do solutions containing dissolved salts. The saturated aqueous solution of tributyl phosphate was selected as a test fluid to

TABLE 2. COMPOSITION OF HAZARDOUS WASTES IN EXPOSURE TESTS

Type of waste		pH, water phase	Solids, % Total	Solids, % Volatile	Organic liquid phase, %
Acidic	"HFL"	4.8	2.48	0.9	0
	"HNO_3, HF, HOAC"	1.5	0.77	0.12	0
Alkaline	"Slopwater"	12.0	22.43	5.09	0
	"Spent caustic"	11.3	22.07	1.61	0
Lead	"Low lead gas washing"	7.2	1.52	0.53	104
	"Gasoline washwater"	7.9	0.32	0.17	1.5
Oily	"Aromatic oil"	...	...	...	100
	"Oil pond 104"[a]	...	~36	~31	89
	"Weed oil"	7.5	1.81	1.00	21
Pesticide	"Weed killer"	2.7	0.78	0.46	0

[a] Solid phase was 11%.

simulate the presence of dissolved organic material in a waste fluid.

RESULTS OF EXPOSURE TO HAZARDOUS WASTES

Incompatibility of some of the liners with particular wastes was shown in the screening tests and consequently several liner-waste combinations were deleted. The only admix liner material that was placed below the acid waste was the hydraulic asphalt concrete. Neither of the two oily wastes was placed on the asphaltic liners; however, the lead waste, which contained a light, oily fraction, was placed on these liners. The performances of the individual liners are discussed below.

Compacted Fine-Grain Soil

All of the wastes, except the nitric acid waste, were placed above the compacted fine-grain soil liner. Seepage below all of the liners took place. The amount of seepage was measured and the respective pH, conductivity, and percent total solids were determined. The following observations are made with respect to the seepages through the soil liners:

a. The rate of seepage is 10^{-8} to $10^{-7} cm \cdot sec^{-1}$ which compares favorably with the permeability of the soil measured in the laboratory permeameter. There is some variation in the amount of seepage collected below the liner which may reflect permeability differences, perhaps due to density of the soil.

b. The fluids being collected after more than three years of exposure still continue to be essentially neutral and to have high solids content (mostly salt) and electrical conductivity.

c. There is a downward trend in solids content of the seepages collected under the pesticide and lead wastes, but the seepage under the spent caustic waste continues to be 23% solids.

One set of the soil liners was removed and tested. The permeability of a specimen taken from the cell containing the soil and the aromatic oil waste was determined using a "back-pressure" permeameter. The sample was collected from a depth of seven to ten inches below the surface of the soil, i.e. from that part of the soil which was not penetrated by the oil. The three consecutive values obtained were: 1.83×10^{-8}, 2.43×10^{-8}, and 2.60 x 10^{-8} cm·sec^{-1}. These figures indicate the low permeability of the soil, which had a bulk density of 1.318 g cm^{-3} and a saturation degree of 101%.

Analyses for trace metals were made of the soils which were below the lead waste, Oil Pond 104, and the aromatic oil. The testing included determination of pH and heavy metal content (cadmium, chromium, copper, magnesium, nickel, and lead) on samples collected at different depths in the cells.

With the exception of the liner exposed to spent caustic, the pH of the soil liner was not significantly altered by the wastes. The pH of these samples was in the range of 7.0 to 7.6; the ratio, soil:solution, was 1:2 with 0.01N $CaCl_2$ being the equilibration solution.

In the case of the spent caustic, the pH values were around 9.0 for samples collected in the first two to three centimeters, which concurs with our previous findings that, over the exposure period of 30 months, the wetting front of the wastes penetrated the soil to a depth of only three to five centimeters.

The heavy metals distribution, as indicated by the analysis, shows, in the case of the lead, only a shallow contamination of the soil. Similar results were obtained on all six heavy metals in the case of the soil below the Oil Pond 104 waste.

Admixes

Soil Cement

All of the wastes except the acid waste were placed on the soil cement liner. No seepage occurred through the liner during the 30 months of exposure.

One set of the soil cement lining materials was recovered after 625 days of exposure to the various wastes and the individual linings were cored and tested for compressive strength. In all cases, compressive strength of the exposed soil cement was greater than that of the unexposed material. There was some blistering of the epoxy asphalt coating which was applied to one-half the surface of each specimen.

Modified Bentonite and Sand

Two types of modified bentonites were used in admix liners in ten cells. One type allowed somewhat less seepage than the other. There was measurable seepage in seven of the ten cells and one failed allowing the waste (Oil Pond 104) to come through the liner.

Irrespective of the type of waste above the liner, the quality of the seepage was not greatly different among the samples collected. The seepages collected below the pesticide waste on both types of modified bentonite liners were similar.

When the spacers containing the bentonite-sand were sampled, it was found that there had been considerable channeling of the wastes into these liners. There was no channeling at the walls of the spacers, which indicates that the epoxy seal at the top of the liner was effective in preventing wall effects and by-passing of the liner.

The bentonite admixes are probably not satisfactory for the types of waste that were used in this study. The use of a cover on the bentonite layer to produce an overburden would probably reduce the channeling effect.

Hydraulic Asphalt Concrete

Liner specimens of hydraulic asphalt concrete were placed under four non-oily wastes.

This lining material functioned satisfactorily under the pesticide and spent caustic wastes, but failed beneath the nitric acid waste. The failure arose primarily from the failure of the aggregate which contained calcium carbonate; also, the asphalt hardened considerably.

In the case of the lead waste, the asphalt absorbed much of the oily constituents of the waste and became "mushy". Some staining of the gravel below the asphalt liner occurred.

Duplicate cells containing the hydraulic asphalt concrete and the lead waste are still functioning without seepage.

Sprayed-On Membrane Liner Based on Emulsified Asphalt and Nonwoven Fabric

This membrane was placed under only three of the six wastes: pesticide, spent caustic, and lead. The acid waste was excluded because it caused severe hardening of the asphalt, and the oil wastes were excluded because of the high mutual solubility of the asphalt and the wastes.

The asphalt membrane functioned satisfactorily with the pesticide and spent caustic wastes; however, when the cell containing the lead waste was dismantled, the gravel below the liner was wet and stained brown. This result indicates that some seepage took place.

Polymeric Membrane Liners

All of the flexible polymeric membranes survived the exposure testing, except the polyester elastomer which failed on exposure to the nitric acid waste. This material completely lost its elongation and cracked in the cell at the edges of the liner. The nitric acid waste caused several of the cells to leak due to corrosion of the steel walls through pinholes in the epoxy coating, particularly at the welds between the walls and the flanges.

The membrane liners that were removed from the cells were photographed, inspected visually, and subjected to the following tests:

- Determination of volatiles and extractables.
- Tensile properties in machine and transverse directions.
- Hardness.
- Tear strength in machine and transverse directions.
- Puncture resistance.
- Seam strength.

The tests of the membranes were performed soon after their removal from the wastes and while they were still swollen.

Determining the volatiles and extractables of the exposed liner supplies information with respect to the amount of waste that is absorbed by the liner and the amount of the original compound that is leached out during the exposure. The volatiles were run first by determining the loss in weight of a two inch diameter disk heated for two hours at 105°C. The extractables were determined on specimens that had been devolatilized by exposure to circulating air at room temperature and heating at 105°C. The appropriate solvent was used in order to extract the nonpolymeric fraction without dissolving the polymer.

The volatiles test was also used to verify the direction of the grain of the membrane which was introduced during manufacture. (On heating, polymeric liners shrink more in the machine direction.) Some physical properties are significantly affected by grain direction, a factor which was not considered in the preparation of some of the early specimens for exposure.

The tensile properties that are of interest in the assessment of the effects of exposure are:

- Tensile strength at break.
- Elongation at break.
- Stresses at 100% and 200% elongation.
- Tensile set.

Because of the grain introduced in most membrane liners during manufacture tensile properties must be measured in both machine and transverse directions.

Tensile strength is an important quality of a polymer and is often a good measure of the quality of the compound of the polymer. Tensile *per se* does not necessarily reflect on performance when various materials are compared. Many compound ingredients, e.g. fillers and oils reduce tensile; also, on aging, tensile strength generally drops.

Elongation, which is an important property in the functioning of many rubber and plastic products, appears to be an important property for liners. The loss of elongation in service either by loss of plasticizer or by excessive swelling could result in breakage, since the membrane may not tolerate an extension beyond which it was designed.

The stresses at 100% and 200% elongation are measures of the stiffness or modulus of a rubber or plastic compound. It is affected by the amount of swelling that takes place and by crosslinking or oxidation that might take place in the rubber. This property is related to hardness.

Tensile set is the stretch that is retained in a specimen after it has been tensile tested. The value gives an indication of the creep that a material might take during service to accommodate stress.

Tear strength and puncture resistance are two properties of membranes that are important in their installation in the field. Tear resistance can also be important in exposed liners, as can puncture strength, particularly on prolonged exposure of liners under a load or on a soil surface.

Seams, particularly those made in the field, can be a source of problems during installation and service. Specimens of the recommended seams should be subjected to exposure testing similar to that given the membrane and preferably under mechanical stress conditions.

Results of the Primary Exposure Tests

All of the tests discussed above were performed on the primary liner specimens. Of particular interest are the volatiles, extractables, and retention of ultimate elongation after exposure to the various wastes. The results for the tests of these properties are presented in Tables 3-5, respectively.

All of the materials that were exposed absorbed volatiles, primarily water, and, in the case of the lead waste, some low molecular weight hydrocarbons. The pesticide waste had a low ion concentration which resulted in high absorption of water. The lead waste contained minor amounts of oily material which was absorbed by the neoprene. The two liners that absorbed the least amount of volatile materials were the elasticized polyolefin and the polyvinyl chloride membranes. The neoprene, chlorinated polyethylene, and chlorosulfonated polyethylene membranes absorbed the most and sustained the greatest changes in properties.

In most cases, the "extractables" of the exposed liners were higher than the extractables of the respective unexposed liner materials. Exceptions were the polyvinyl chloride, the chlorinated polyethylene, and, to a minor extent, the neoprene, all of which had been immersed in lead waste. The plasticizer in these

TABLE 3. VOLATILES[a] OF PRIMARY POLYMERIC MEMBRANE LINER SPECIMENS AFTER EXPOSURE TO SELECTED WASTES

Liner data		Compound data		Volatiles, % Waste and exposure time in days						
Polymer	Number[b]	Type[c]	Extractables[d], %	Unexposed	Pesticide 1260 d	HNO_3 1270 d	Spent caustic 1250 d	Lead 1340 d	Oil Pond 104 1360 d	Aromatic oil ...
Butyl	57R	VZ	6.4	0.29	4.8	11.5	1.4	3.5	...	...
CPE	77	TP	9.1	0.00	7.9	13.2	2.8	19.2	10.1	...
CSPE	6R	TP	3.8	0.29	9.7	7.2	5.8	11.4	10.3	...
ELPO[e]	36	TP	5.5	0.15	(f)	5.3	(f)	1.5	5.1	(f)
EPDM	26	VZ	18.2	0.50	6.3	12.0[g]	1.3	5.3	...	...
Neoprene	43	VZ	13.9	0.45	13.6	...	5.7	17.5	21.3	...
Polyester	75	TP	2.7	0.26	2.9	7.4[h]	0.9	1.7	2.6	(f)
PVC	59	TP	35.9	0.26	3.6	...	1.8	4.4	4.2	(f)

[a] Percent weight loss after 2 h at 105°C.

[b] Serial number of liner set by Matrecon; R = Fabric reinforced.

[c] Type = Vulcanized (VZ) or thermoplastic (TP).

[d] After volatiles were removed.

[e] ELPO = Elasticized polyolefin.

[f] Specimens still under exposure to waste.

[g] Exposure time = 1150 days.

[h] Exposure time = 509 days.

TABLE 4. EXTRACTABLES[a] OF PRIMARY POLYMERIC MEMBRANE LINER SPECIMENS AFTER EXPOSURE TO SELECTED WASTES

Liner data		Compound data		Extractables, % Waste and exposure time in days					
Polymer	Number[b]	Type[c]	Extractables[a], %	Pesticide 1260 d	HNO_3 1220 d	Spent caustic 1250 d	Lead 1340 d	Oil Pond 104 1360 d	Aromatic oil ...
Butyl	57R	VZ	6.4	7.6	8.7	7.9	7.9	...	...
CPE	77	TP	9.1	9.4	10.6	9.1	7.2	17.0	...
CSPE	6R	TP	3.8	5.4	4.6	3.8	6.0	9.5	...
ELPO[d]	36	TP	5.5	(e)	7.1	(e)	8.1	20.7	(e)
EPDM	26	VZ	18.2	25.2	22.8[f]	24.0	26.0	...	...
Neoprene	43	VZ	13.9	16.1	...	13.7	12.2	15.9	...
Polyester	75	TP	2.7	5.8	13.59	3.3	5.4	7.3	(e)
PVC	59	TP	35.9	33.4	(e)	35.6	22.5	30.0	(e)

[a] After volatiles were removed

[b] Serial number of liner set by Matrecon; R = Fabric reinforced.

[c] Type = Vulcanized (VZ) or thermoplastic (TP).

[d] ELPO = Elasticized polyolefin.

[e] Specimens still under exposure to waste.

[f] Exposure time = 1150 days.

[g] Exposure time = 509 days.

TABLE 5. RETENTION OF ULTIMATE ELONGATION[a] OF PRIMARY POLYMERIC LINER SPECIMENS AFTER EXPOSURE TO SELECTED WASTES

Liner data		Compound data			Ultimate elongation, % retention Waste and exposure time in days					
Polymer	Number[b]	Type[c]	Extractables[d], %	Original elongation[e], %	Pesticide 1260 d	HNO_3 1220 d	Spent caustic 1250 d	Lead 1340 d	Oil Pond 104 1360 d	Aromatic oil ...
Butyl	57R	VZ	6.4	70	77	419	142	108	...	...
CPE	77	TP	9.1	405	90	88	115	84	89	...
CSPE	6R	TP	3.8	235	88	83	68	81	75	...
ELPO[f]	36	TP	5.5	665	(g)	96	(g)	106	79	(g)
EPDM	26	VZ	18.2	450	103	79[h]	95	106	...	...
Neoprene	43	VZ	13.9	320	84	...	95	75	92	...
Polyester	75	TP	2.7	575	87	<1[i]	87	90	90	(g)
PVC	59	TP	35.9	385	93	(g)	95	106	122	(g)

[a] Ultimate elongation = The average of the values in both machine and transverse directions.

[b] Serial number of liner set by Matrecon; R = Fabric reinforced.

[c] Type = Vulcanized (VZ) or thermoplastic (TP).

[d] After volatiles were removed.

[e] Original elongation = Ultimate elongation of unexposed material.

[f] ELPO = Elasticized polyolefin.

[g] Specimens still under exposure to waste.

[h] Exposure time = 1150 days.

[i] Exposure time = 509 days.

materials leached into the wastes resulting in a lower extractables content.

The elongation retention data presented in Table 5 show almost complete loss of elongation by the polyester elastomer in the nitric acid waste. The other lining materials retained most of their respective elongations. The CSPE showed the greatest loss other than the polyester elastomer, retaining 68% of its original elongation.

Results of Immersion Testing

Tables 6 and 7 present results of the immersion of 12 polymeric liner materials in 8 wastes. Five of the liners duplicate the primary liners and 6 of the wastes are the same as those used in the primary exposure test. The data on the weight increases of the liners during immersion are presented in Table 6. Table 7 presents the data on the changes in extractables of the immersed specimens during the exposure period. The extractables are determined on the liners after the volatiles are removed and reflect the amount of nonvolatile material that is either gained or lost by the immersed specimens. Most specimens absorbed oil when immersed in Oil Pond 104, while the PVC liners lost plasticizer to this waste.

A supplemental study was performed on three polymers that are partially crystalline, i.e. high-density polyethylene, low-density polyethylene, and polypropylene (PP), and one composition based on vulcanized CPE. None of the crystalline sheets are specifically liner materials. They were selected for this test because membranes based on these polymers were potentially suitable for lining waste impoundments, and because they have comparable thicknesses to most of the membrane materials being tested. LDPE in the 10-mil version has been used for lining canals and water impoundments: recently, HDPE was introduced as a commercial lining material for chemical waste impoundments. The vulcanized CPE is not a commercial material either, and, if used as a liner, would require the development of an adhesive system. Results of immersion tests of these materials for 99 days are reported in Table 8.

The absorption of wastes by these four materials is significantly less than observed with the 12 membranes discussed above. Minor changes in physical properties were also observed, thus indicating their good chemical resistance. Additional specimens of these four materials continue to be exposed and will be tested later.

TABLE 6. ABSORPTION OF WASTE BY POLYMERIC MEMBRANE ON IMMERSION IN SELECTED WASTES
(Data in change in weight, percent)

Liner data		Compound data		Waste and immersion time in days							
Polymer	Number[a]	Type[b]	Extractables[c], %	Pesticide 807 d	HNO_3 751 d	HF 761 d	Spent caustic 780 d	Lead 786 d	Oil Pond 104 752 d	Aromatic oil 761 d	Weed oil 809 d
Butyl	44	VZ	11.8	1.6	3.8	3.7	0.8	28.7	103.9	31.2	64.2
CPE	77	TP	9.1	12.7	19.9	12.9	1.1	118.9	36.9	226.4[d]	ND[e]
CSPE	6R	TP	3.8	17.3	10.0	9.0	4.3	120.7	49.5	105.2	368.4
CSPE	55	TP	4.1	15.7	10.9	7.7	3.3	116.2	55.0	110.5	347.5
ELPO[f]	36	TP	5.5	0.5	7.6	1.1	0.6	17.0	28.9	29.4	38.1
EPDM	83R	TP	18.2	4.5	4.2	3.1	1.6	24.8	26.5	19.8	84.4
EPDM	91	VZ	23.6	20.4	50.9	23.9	1.3	34.7	84.7	34.2	76.2
Neoprene	90	VZ	21.5	11.4	17.4	12.0	1.5	59.1	26.3	142.6	89.3
Polyester	75	TP	2.7	4.2	6.4	2.0	1.5	7.4	8.5	16.6	14.7
PVC	11	TP	33.9	5.1	22.1	18.1	0.4	-1.5	-10.4	18.5	15.3
PVC	59	TP	35.9	1.0	-6.1	0.9	-0.9	7.4	-0.5	28.9	24.7
PVC	88	TP	33.9	1.6	28.2	14.3	1.1	-5.2	-9.8	14.1	25.2

[a] Serial number of liner set by Matrecon; R = Fabric reinforced.

[b] Type = Vulcanized (VZ) or thermoplastic (TP).

[c] After volatiles were removed.

[d] Specimen partially dissolved in the waste; value reported is an approximation.

[e] ND = Specimen was lost; there is some indication that it dissolved in the waste.

[f] ELPO = Elasticized Polyolefin.

TABLE 7. CHANGE IN EXTRACTABLES OF FLEXIBLE MEMBRANE LINERS DURING EXPOSURE IN WASTES

Liner data		Compound data		Waste and immersion time in days							
Polymer	Number[a]	Type[b]	Extractables[c], %	Pesticide 807 d	HNO_3 751 d	HF 761 d	Spent caustic 780 d	Lead 786 d	Oil Pond 104 752 d	Aromatic oil 761 d	Weed oil 809 d
Butyl	44	VZ	11.8	...	-0.6	-1.1	-0.8	+4.3	+15.5	+10.7	+2.8
CPE	77	TP	9.1	...	+2.5	+1.0	+0.1	+6.1	+8.0	ND[d]	ND[e]
CSPE	6R	TP	3.8	...	0	0	0	+0.8	+10.4	+22.0	+12.2
CSPE	55	TP	4.1	...	-0.1	-0.5	+0.1	-0.4	+9.8	+21.0	+10.0
ELPO[f]	36	TP	5.5	...	+0.7	+0.4	0	+1.3	+10.0	+13.4	+2.4
EPDM	83R	TP	18.2	...	-0.5	-0.9	-0.2	+2.2	+2.9	+6.0	+0.4
EPDM	91	VZ	23.6	...	+1.2	-0.8	-0.5	+3.9	+8.6	+7.4	+1.2
Neoprene	90	VZ	21.5	...	-1.7	-1.4	-0.5	-1.7	+1.7	+9.4	-12.6
Polyester	75	TP	2.7	...	+7.2	+0.6	0	+0.6	+3.5	+11.5	+3.2
PVC	11	TP	33.9	+0.7	-0.8	-0.6	0	-12.3	-11.6	+2.6	-8.7
PVC	59	TP	35.9	-0.5	-8.0	-0.9	0	-4.5	-4.4	+1.8	-3.1
PVC	88	TP	33.9	-1.1	-0.3	-1.5	-0.7	-11.7	-14.8	+1.9	-9.6

[a] Serial number of liner set by Matrecon; R = Fabric reinforced.

[b] Type = Vulcanized (VZ) or thermoplastic (TP).

[c] After volatiles werre removed.

[d] ND = Specimen partially dissolved in the waste.

[e] ND = Specimen was lost; there is some indication that it dissolved in the waste.

[f] ELPO = Elasticized Polyolefin.

TABLE 8. ABSORPTION OF WASTE BY THREE CRYSTALLINE POLYMERS AND A VULCANIZED CPE COMPOSITION

(Data in change in weight, percent)

Liner data			Waste and immersion time in days					
Polymer	Number[a]	Type[b]	HNO_3 99d	HF 99d	Spent caustic 99d	Aromatic oil 99d	Weed oil 99d	Slopwater 99d
CPE	100	VZ	...	+4.2	...	+11.9	...	-0.5
HDPE	105	XL	+0.1	+0.05	+0.2	+4.4	+6.4	+0.2
LDPE	108	XL	-0.3	-3.3	+0.1	+8.5	+10.7	+3.5
PP[c]	106	XL	+0.1	+0.05	+0.2	+0.4	+1.4	+0.1

[a] Serial number of liner set by Matrecon.

[b] Type = Vulcanized (VZ) or crystalline (XL).

[c] PP = Polypropylene.

SWELLING OF POLYMERIC MEMBRANES

The polymeric compounds that have been studied in this project can be classified in the following four types:

- Vulcanized elastomers, e.g. butyl rubber, neoprene, EPDM, CSPE, CPE, ECO, nitrile rubber, and blends.
- Thermoplastic elastomers (TPE), e.g. CSPE, CPE, polyolefins, and blends.
- Thermoplastics, e.g. plasticized PVC, and PVC blends with selected elastomers.
- Crystalline polymers (thermoplastic), e.g. LDPE and HDPE.

Some of the polymers are used in both crosslinked and thermoplastic versions. For example, lining materials of CSPE and EPDM have been manufactured in both crosslinked and thermoplastic versions.

On exposure to fluids, most polymeric materials, whether they are crosslinked or not, will tend to swell and change in some properties. The major factors involved in the swelling of polymeric materials are:

- Solubility parameter.
- Crosslinking of polymer.
- Crystallinity of polymer.
- Chemical stability.
- Soluble constituents in compound.

The solubility parameter (Hildebrand and Scott, 1950) is used by polymer scientists to measure the similarity in chemical characteristics of polymers such as are used in the lining materials. This parameter is related to the polarity of materials. A polymer which has a solubility parameter value close to that of the fluid medium in which it is placed, will swell and sometimes dissolve. For example, a hydrocarbon rubber like natural rubber will swell and dissolve in a hydrocarbon such as gasoline. On the other hand, a highly polar polymer, such as polyvinyl chloride or nitrile rubber, will not dissolve in gasoline.

Crosslinking a polymer or a rubber limits its swelling in solvents. Polymer scientists use the swelling of a crosslinked rubber as a measure of the degree of crosslinking - the greater the crosslinking, the less the swelling. This effect is pronounced in such rubbers as CSPE and CPE, liners of which are available in both vulcanized and unvulcanized versions.

Crystallinity in a polymer acts much like crosslinking to reduce the ability of a polymer to dissolve. Highly crystalline polymers, such as high-density polyethylene, will not dissolve in gasoline, even though they are basically similar in chemical composition. Such high density polymers are finding considerable use in containers for a wide range of solvents and chemicals.

The soluble constituents of a rubber compound have a strong bearing on the ability of that material to swell. Most commercial polymers contain minor amounts of solubles, e.g. salt, which are used in the manufacture of the polymer. Soluble constituents can also arise from ingredients which are used in the compounding. Swelling is a result of the diffusion of water into the compound by osmosis.

The effects that the first three factors have on the swelling of liner materials is illustrated in Figure 4. The swelling of the thermoplastic type of material in a fluid with which it is somewhat compatible is represented in Curve A, which indicates that the material will continue to swell with time and that no real plateau is reached.

The swelling of crosslinked material is represented in Curve B, in which the swelling reaches a plateau and changes

TYPES OF SWELLING OF POLYMERIC MEMBRANE LINERS

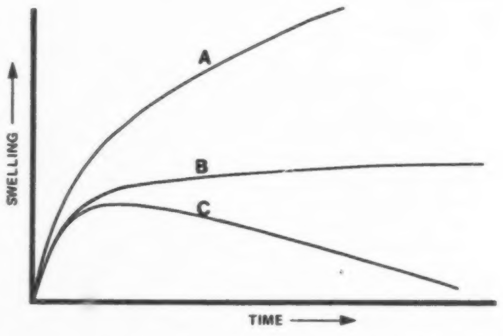


Figure 4. Types of swelling of polymeric membranes.

only slightly with time. The level of the plateau is determined by the degree of slinking and by the solubility parameters of the waste fluid and the polymer.

Curve C represents the case of a plasticized thermoplastic or an oil-extended rubber in which the plasticizer is leached from the polymer. In this case, there is an initial swelling followed by a reduction in swelling. In some cases, there can be a shrinkage of the liner due to the loss of plasticizer or oil.

In selecting polymer and rubber compounds for service in a liquid medium, a designer generally selects materials which have low or negligible swell. Swelling of a compound usually has adverse effects which will make the product unserviceable. Some of the major effects of swelling generally are:

- Softening and possibly dissolving.
- Loss of tensile and mechanical strength.
- Loss in elongation.
- Increased permeability.
- Increased potential of creep.
- Greater susceptibility to polymer degradation.

All of these effects are adverse with respect to liner performance. Swelling, therefore, is a valuable indicator of the compatibility of a liner to a waste.

Shrinkage can also be a measure of compatibility for liner compositions that are highly plasticized. For example, in the case of highly plasticized PVC compounds, the plasticizer can leach and diffuse out of the polymer compound, leaving it stiff and brittle.

IMMERSION OF POLYMERIC MEMBRANES IN AN AQUEOUS SOLUTION OF TRIBUTYL PHOSPHATE

The immersion of a series of widely different polymeric membrane liners in a saturated aqueous solution of tributyl phosphate demonstrates the effect of a very low (0.40%) concentration of organic chemical constituents on the swelling and properties of a membrane liner during prolonged exposure. Tributyl phosphate was selected for this experiment because of its slight solubility in water, its low volatility, and its phosphorus content which can be used to follow the migration of the plasticizer. Results of exposing specimens of 12 polymeric membrane linings, all without fabric reinforcement, are presented in Table 9. The sheetings include thermoplastic, vulcanized, and crystalline types of polymeric membranes.

TABLE 9. EFFECTS ON PROPERTIES OF LINER MATERIALS[a] ON IMMERSION IN A SATURATED SOLUTION OF TRIBUTYL PHOSPHATE IN DEIONIZED WATER (0.4% TBP) FOR 522 DAYS

Polymer	Butyl	CPE	CPE	CSPE	ELPO[b]	EPDM	Neoprene	PESE[c]	PVC	HDPE	LDPE	PP
Type of compound	VZ	TP	VZ	TP	TP	VZ	VZ	TP	TP	XL	XL	XL
Matrecon number	44	77	100	55	36	91	90	75	59	105	108	106
Initial thickness, mils	63	30	36	33	23	32	35	7	33	32	31	33
Analytical properties:												
Weight gain, %	21.9	107.2	34.4	31.6	6.7	5.2	41.4	4.5	46.2	0.56	0.51	0.18
Extractables, original, %	11.8	9.1	...	4.1	5.5	23.6	21.5	2.7	35.9	...	...	...
Extractables, exposed, %	...	...	...	...	...	...	...	...	...	...	...	...
Gain in volatiles, %	2.2	42.2	19.7	20.7	2.1	4.3	24.8	4.1	11.9	0	0	0
Physical properties[d]:												
Final thickness, mils	64.3	47.9	40.9	37.9	20.2	36.8	43.5	6.6	36.4	31.5	30.9	32.2
Tensile strength, % retention	107	10	63	48	48	93	49	89	31	88	104	97
Elongation at break, % retention	115	155	79	79	74	106	82	101	89	101	102	105
Stress at 100% elongation, % retention	74	6	46	80	70	81	15	90	28	92	103	110
Tear resistance, % retention	...	14	29	39	79	105	34	90	23	77	81	270
Hardness change, points	-2	-60	-20	-14	-3	-1	-25	-10[e]	-33	-1	-20	-2
Puncture test:												
Stress, % retention	73	20	85	112	101	107	66	77	48	101	92	94
Elongation, % retention	126	127	125	131	142	111	119	100	133	107	108	42

[a] All materials are unreinforced.

[b] Elasticized polyolefin.

[c] PESE = Polyester elastomer.

[d] Data for tensile, elongation, S-100, and tear are the averages of measurements made in both machine and transverse directions.

[e] Due to curling of sample, magnitude of change as reported is probably too great.

The crystalline materials are not commercial liner sheeting, but two, HDPE and LPDE, are available as liner membranes. These three sheetings were used in this exposure test in order to be able to make comparisons at the same thickness with most of the other polymeric materials. The immersion exposure was for 522 days and the following parameters were measured: weight change, extractables, volatiles (water), tensile strength, elongation at break, modulus, hardness, tear, and puncture resistance.

The thermoplastics, PVC, CPE, and CSPE, increased significantly in weight and lost considerably in tensile strength and hardness. The vulcanized CPE sustained less change than did the thermoplastic CPE composition. The neoprene liner, though vulcanized, swelled considerably and lost in tensile strength and hardness. The butyl and EPDM liners, also vulcanized, did swell to some extent and sustained only modest losses in properties.

Of particular interest are the low swelling and loss in properties incurred by the crystalline polymers, thus showing the good chemical resistance of these materials.

Immersion of the second set of specimens in this test is continuing and a full analysis is being made of the swollen exposed materials to determine the composition of the extractables.

DISCUSSION

Results generated in the project indicate that, within present liner technology, materials are available which are suitable to use to line impoundments of a great range of hazardous wastes. Certainly, materials are available to handle the wastes that were used in this project. On the other hand, no single available lining material appears to be suitable for long-term impoundment of all wastes. There is considerable variation in the compatibility of wastes and liners. Generally, wastes that are highly ionic, contain salts, strong acids, or strong bases, can be aggressive to soils, soil cement, aggregate, hydraulic asphalt concrete, and to some of the membranes, particularly those containing plasticizers. Wastes which have organic components can be aggressive toward the membrane liners by swelling the polymer compounds and toward asphaltic materials by dissolving them. In particular, the oily wastes cause swelling and loss of physical properties in the membrane liners and the asphaltic materials.

It is quite apparent, therefore, that compatibility studies must be performed prior to the selection of the liners for handling specific wastes and that, once the selection has been made and the site lined, the waste that is being impounded should be monitored closely to insure that only proper waste is added. In making the compatibility studies, contact of samples of the liner materials under consideration and the waste to be impounded should be as long as possible. Our tests show that, in many cases, no leveling off in the effects of the waste on the membrane occurs with time. Such behavior means that, for long-term exposure, there can be a continuing change of the liner with time.

In the case of the polymeric membrane liners, some of the more useful tests and properties which appear to be promising for assessing the suitability of a given liner for use with a given waste are:

1. The measurement of swelling of the membrane materials in the wastes or in the leachate of the wastes.
2. The loss of elongation, with time, of the polymeric membranes when in contact with the waste or its leachate.
3. The use of the pouch test for measuring the compatibility of the liners and the waste and the permeability of the liner to the constituents of the waste.

The laboratory tests that are proposed need continuous comparison with long-term exposures in order that they can be used to assess liners and predict their long-term performance in service. Such correlation requires observation of liners in actual service over extended periods of time.

The analyses and characterization of wastes with respect to those constituents that are aggressive to lining materials will be useful in the selection of liners.

In developing a new liner material for use in the lining of waste impoundments, it is quite obvious that the new material under development should be tested under a variety of environmental conditions. Furthermore, it would appear desirable to consider composite types of liners involving two or more materials for use in impounding the more aggressive and polluting types of wastes.

ACKNOWLEDGMENT

The research which is reported in this paper is being performed under Contract 68-03-2173, "Evaluation of Liner Materials Exposed to Hazardous and Toxic Sludges", with the Environmental Protection Agency, Municipal Environmental Research Laboratory, Cincinnati, Ohio. The support and guidance of Mr. R. E. Landreth, Project Officer, is gratefully acknowledged.

REFERENCES

Fong, M. A., and H. E. Haxo. 1981. Assessment of Liner Materials for Municipal Solid Waste Landfills. Seventh Annual Research Symposium, Philadelphia, PA. (See these proceedings).

Haxo, H. E. 1976. Evaluation of Selected Liners when Exposed to Hazardous Wastes. In: Proceedings of the Hazardous Waste Research Symposium, Residual Management by Land Disposal. EPA-600/9-76-015. U. S. Environmental Protection Agency, Cincinnati, Ohio.

Haxo, H. E. 1978. Interaction of Selected Lining Materials with Various Hazardous Wastes. In: Proceedings of the Fourth Annual Research Symposium. EPA-600/9-78-016. U. S. Environmental Protection Agency. Cincinnati, Ohio.

Haxo, H. E. 1980a. Interaction of Selected Liner Materials with Various Hazardous Wastes. In: Disposal of Hazardous Waste, Proceedings of the Sixth Annual Research Symposium. EPA-600/9/80-010. U. S. Environmental Protection Agency. Cincinnati, Ohio.

Haxo, H. E. 1980b. Laboratory Evaluation of Flexible Membrane Liners for Waste Disposal Sites. Presented at the 117th Meeting of the Rubber Division. American Chemical Society. Las Vegas, Nevada.

Haxo, H. E., R. S. Haxo, and R. M. White. 1977. Liner Materials Exposed to Hazardous and Toxic Sludges. First Interim Report. EPA-600-2-77-081. U. S. Environmental Protection Agency. Cincinnati, Ohio.

Haxo, H. E. 1981a. Testing of Materials for Use in Lining Waste Disposal Facilities. Presented at ASTM Symposium on Hazardous Solid Waste Testing. Ft. Lauderdale, FL.

Haxo, H. E., et al. 1981b. Liner Materials Exposed to Hazardous and Toxic Sludges. Final Report. EPA-68-03-2173. In preparation.

Hildebrand, J. H., and R. L. Scott. 1964. The Solubility of Nonelectrolytes. Third Edition. Dover Publications, Inc., New York. 488 pp.

Matrecon, Inc. 1980. Lining of Waste Impoundment and Disposal Facilities. SW-870. U. S. Environmental Protection Agency. Washington, DC. 385 pp.

INSTALLATION PRACTICES FOR LINERS

David W. Shultz
Michael P. Miklas, Jr.
Southwest Research Institute
6220 Culebra Road
San Antonio, Texas 78284

ABSTRACT

Southwest Research Institute is presently conducting a study to identify current methods and equipment used to (1) prepare supporting subgrade and to (2) install liners at various waste disposal facilities in the United States. Information obtained during the site visits includes:

(1) Methods and equipment used to prepare the subgrade;

(2) Methods and equipment used to place the liner material;

(3) Design and construction considerations; and

(4) Any special problems encountered during installation and subsequent solutions.

The subgrade preparation and installation of three generic types of liner materials are discussed in this paper. Photographs depicting various construction and placement activities are presented.

INTRODUCTION

The use of surface impoundments and landfills to store, treat and/or dispose of unwanted materials has been and continues to be common practice for industry and municipal agencies since these types of facilities have proven to be cost effective solutions to treatment and disposal problems. Recent studies have shown that the use of such facilities can result in subsurface migration of hazardous materials into groundwater resources.

The Resource Conservation and Recovery Act of 1976 and proposed EPA regulations will require positive control of subsurface migration of contamination from many of these facilities where hazardous materials are stored. Future treatment and/or disposal sites will likely have to be designed to prevent groundwater contamination. It is likely that impermeable liners with high integrity will find increased usage in the future.

The proper planning, design and construction of surface impoundments and/or landfills designed to contain hazardous wastes involve numerous steps, including the following: (1) defining facility function and geometry; (2) selection of a liner material which is compatible with the material to be stored or treated; (3) planning suitable subgrade preparation, proper liner installation, adequate seepage monitoring and collection provisions; and (4) developing appropriate post-installation operation and maintenance planning.

This study, which addresses subgrade preparation and liner placement, has the following objectives:

(1) To identify current subgrade preparation procedures and equipment used to build surface impoundments and landfills;

(2) To identify methods and equipment utilized to install various liner

materials; and

(3) To identify special problems which should be considered during the planning, construction, and operation of such facilities.

The following generic types of liners are intended to be included in this study: (1) compacted native soils (clays); (2) admixes (asphalt, concrete and soil cement); (3) polymeric membranes (rubber and plastic sheeting); (4) sprayed-on linings; (5) soil sealants; and (6) chemical absorbents. This paper discusses three of these types, i.e., asphalt, soil sealant, and sprayed-on liners.

SITE 1 - ASPHALT LINED LANDFILL

Background

Site 1 is a municipal landfill begun approximately 5 years ago. Presently, the landfill covers 20 acres with an average compacted fill depth of 100 feet. The site is situated in a ravine. The ravine is 300-600 feet across at the top of the hill and it gradually widens toward the bottom. Construction was initiated at the upper end and is progressing downward. Future plans call for the filling of the entire ravine, resulting in a fill covering 170 acres.

The landfill is lined with a road grade asphalt, approximately 2 inches thick. The liner has been expanded in 5 acre sections as the landfill construction progressed. Standard roadway paving equipment has been used to install the liner. The design of the liner provides for containment of any leachate produced by the fill. Subgrade preparation and liner placement are discussed in the following sections.

Subgrade Preparation

Adequate compaction of subgrade after grading is critical to the integrity of any liner. Sufficient compaction insures that the liner will not be damaged as a result of differential settling. The site was graded to conform to the slope of the ravine. Figure 1 shows the drainage provided at the edge of the compacted subgrade. Note the slope of the subgrade off to the left. The subgrade gradually slopes from this side of the ravine to the other side, where a curb allows any leachate produced to be effectively collected. Surface runoff into the landfill is controlled by the drainage channels surrounding the site. These channels prevent overland flow from entering the fill. Surface drainage from the channels is directed to an erosion control basin. After final grading, 12 inches of specially selected material were recompacted in 6 inch lifts to achieve an optimal subgrade consistency. Standard vibratory rollers were used to produce a subgrade with a modified Proctor density of 90 percent.

Liner Placement

The liner at this site consists of 2 inches of road grade asphalt applied using a standard paving machine, as shown in Figure 2.

The roller shown in Figure 3 was used to compact the asphalt to the desired density.

After the surface cooled, a seal coat was hydraulically applied. The seal coat is intended to protect the asphalt from potential degradation which might occur as a result of exposure to leachate. An asphalt curb was constructed at the edge of the liner to direct leachate to a perforated PVC pipe located inside the curb upon the normal asphalt surface. The PVC leachate collection pipes from each 5 acre section of asphalt are linked together via a manifold system. As new acreage is added, the required new piping is connected to the manifold system. A 20,000 gallon tank stores any leachate produced. Leachate can either be hauled off site or recycled back into the fill. To date, after 5 years of operation, about 13,000 gallons of leachate have been hauled off site.

Cost estimates for the purchase and placement of the asphalt are $15,000 per acre, or $0.35 per square foot. Costs for subgrade preparation are not available.

SITE 2 - SOIL SEALANT LINER

Background

Site 2 is a 62 acre diked wastewater storage impoundment. Excavated material from the impoundment floor was used to construct the dikes. The floor is approximately 40 feet below the elevation of the dikes. Side slopes are three (horizontal) to one (vertical). A swelling bentonite clay modified with a cross-linked polymer was selected as the soil sealant. The native soil is a glacial silt having an unacceptable permeability for the intended use of the impoundment.

Subgrade Preparation

After the site had been graded and recompacted according to design specifications (90% Proctor) the floor of the impoundment was disced to a depth of 4 inches using the dozer drawn disc shown in Figure 4. This was necessary to provide the loose topsoil for blending with the soil sealant. Only one pass of the disc was required. The next step was the application of the bentonite.

Liner Placement

The modified bentonite soil sealant was applied pneumatically by using two air bottle transport trucks equipped with hardware specifically designed for this application. The trucks each carried an air compressor, two storage tanks and associated hardware. Two important additions were a 6 foot wide material distribution boot and an outrigger. These are shown in Figure 5. The boot was attached to the rear of the truck. Soil sealant was forced out through the top of the boot. Internal veins running from the inlet to the bottom allowed an even distribution of material. The bottom skirt helped minimize the loss of material during application. The outrigger shown in Figure 5 allowed the operator immediate and safe access to the material control valves on the side of the truck.

Laboratory tests indicated the desired application rate of soil sealant to be 38 tons/acre or 1.8 pounds/square foot. The required flow rate of soil sealant from the truck as well as the rate of travel were established. Prior to initiating application of the sealant, distance markers were set every 100 feet along the toe of the dike. These markers helped the application crew determine the rate of forward movement of the truck. A strict control of the forward rate of travel was necessary to establish the proper application rate of sealant.

As soon as the marker stakes were set, the application crew began spreading the sealant, as shown in Figure 6. The sealant can be seen to the right of the truck. This operation requires at least two people, a driver and a person to control the application of sealant. To allow continuous spreading during daylight hours, two trucks were utilized. While one truck was spreading the sealant, the second truck was being loaded with sealant stored in six 25-ton capacity silos located on site. The storage capacity in the silos equaled the quantity of material which could be applied in one day by two trucks.

The tarp shown in Figure 7 was used by the on-site quality control engineer to assure the proper quantity of sealant was being applied. The tarp was weighed after the truck passed over it to determine the quantity of sealant material applied in one pass. This test was performed periodically throughout the application procedure.

The disc previously shown in Figure 4 followed the application crew. Approximately eight passes in a crisscross pattern were made to blend the sealant with the soil. The decision as to whether adequate blending had been achieved was made by the application foreman and the on-site technical staff representing the owner of the facility. Adequate blending is necessary for the sealant to reduce permeability to the desired level. The crisscross pattern helped break up clods. Figure 8 shows the disc making a second pass over the soil after sealant had been applied. Freshly applied sealant can be seen to the right in this Figure.

Figure 9 shows an overview of sealant application and discing under way. The sealant truck is to the left. The disc can be seen turning around to make a new pass at the foot of the dike near the end of the impoundment.

On the second day of application, the installation contractor located an 8 foot wide rototiller. This unit was used to complete the blending for the remaining 39 acres. It performed better than the disc, producing a more uniform mixture of soil and bentonite.

Soil sealant was applied to the side slopes by mounting the spreader boot on the blade of a bulldozer. The bulldozer traveled the side slopes horizontally while tethered to the sealant supply truck by a hose. The supply truck was driven around the top of the dike during application on the upper half of the slope, and around the bottom during application on the lower half of the slope.

Upon completion of the soil and sealant blending operation, water was added t the soil on the floor of the impoundment in sufficient quantity to allow compaction t 95 percent of maximum Proctor density. Sufficient moisture was present in the soil on the side slopes to allow the desired compaction without additional water. Due to their steepness, the side slopes were compacted with a rubber tired roller whic could traverse the existing grade. The level floor was compacted with a steel roller. To protect against erosion, slag wa placed along the side slopes.

SITE 3 - SPRAYED-ON LINER

Located at Site 3 was a small test evaporation pond lined with a urethane modified asphalt liner system. The syste is comprised of a polypropylene mat coate with the urethane asphalt material. Loos desertic soil with high permeability was present at the site.

Subgrade Preparation

This impoundment was totally excavatd below the surrounding grade using a small bulldozer. Final grade of the side slopes was approximately three (horizontal) to on (vertical). The surface was smooth, compacted, and free of holes or rocks.

Liner Placement

As previously noted, the liner consisted of a fabric mat to serve a supporting medium and the asphalt material applid to the mat. Figure 10 shows the fabric as positioned over the subgrade. A 6 inch overlap was maintained along all joints. Four inch staples were used to temporarily secure the mat to the soil until the asphalt could be applied.

The mat was extended over the top of the side slopes into an anchor trench 1 foot deep around the perimeter of the impoundment, as shown in Figure 11. The installer was careful to limit the thickness of the mat to no more than three layers.

To prepare the urethane asphalt for spray application, a premix was combined with an activator at a volume ratio of nine to one. Mixing was accomplished in 5 gallon buckets. The mixture was applied using a specialized spray application unit. This unit attached to a 5 1/2 gallon container. A compressor/generator unit was used to provide necessary power for the spray unit. The asphalt was then applied using the hand held spray gun. Sufficient asphalt was applied to achieve saturation of the fabric mat. One coat was applied at the rate of 2 gallons per minute, covering about 8 square yards per minute. This application rate produced the desired membrane thickness of 50 mil. Figure 12 shows the pump unit (to the right) and the spray application using the hand held spray gun. Note that the horizontal seam on the fabric mat behind the applicator has been pre-soaked with the asphalt material. This was done for all fabric seams to assure penetration of material at the critical seam overlaps. In addition, the fabric mat extending into the anchor trenches was coated with asphalt. The installer recommends that the membrane be allowed to cure for 24 hours before being put into service.

SUMMARY

Subgrade preparation requirements and liner placement procedures for three differing processes observed at three installation sites have been presented in this paper. The following table presents a comparactive ranking of various subgrade and placement variables for the three systems. This ranking is based upon personal on-site observations of the authors and available information from manufacturers. Ranking should be utilized for relative/subjective comparisons only.

ACKNOWLEDGEMENTS

This study is being supported by the Solid and Hazardous Waste Research Division, Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio (Grant [illegible]) and Southwest Research Institute, San Antonio, Texas. The authors want to thank Robert E. Landreth, Project Officer, for his guidance and support.

COMPARATIVE RANKING* OF SELECTED SUBGRADE AND PLACEMENT VARIABLES FOR THREE LINER SYSTEMS

	Liner System		
	Asphalt	Urethane Asphalt Over Fabric Mat	Soil Sealant
Degree of Weather Limitations	2	3	1
Level of Crew Experience Needed	3	1	2
Intensity of Subgrade Compaction Necessary	1	2	3
Availability of Materials	1	3	2
Availability of Installation Crews	1	3	2
Intensity of Quality Control Required During Installation	3	1	2
Cost of Materials and Installation	2	1	3

*1 = highest
3 = lowest

Figure 1. Drainage channel to divert surface water away from an asphalt lined landfill.

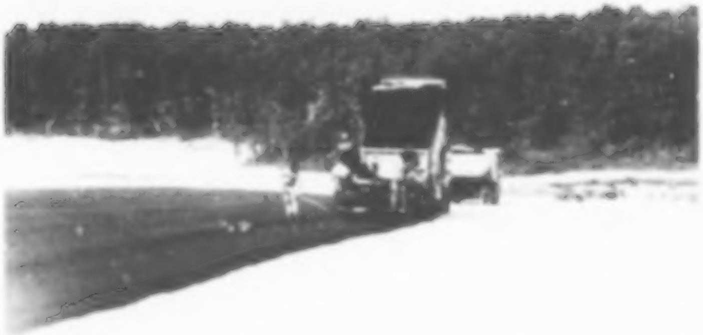


Figure 2. Asphalt paving machine installing an asphalt liner at a landfill site.

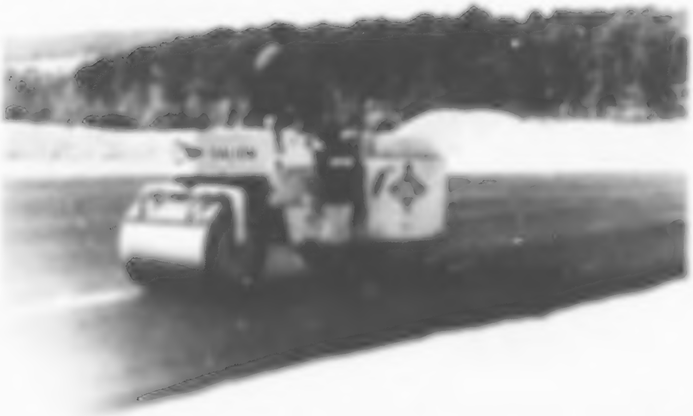


Figure 3. Finishing roller at work on an asphalt liner.

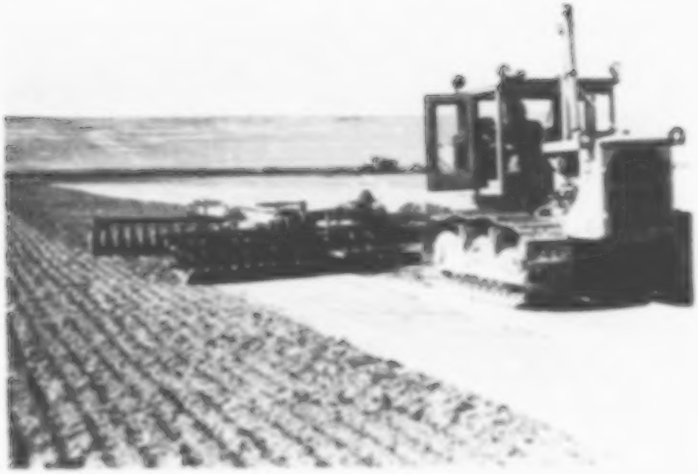


Figure 4. Disc used to prepare soil for the application of a polymer modified Wyoming bentonite.

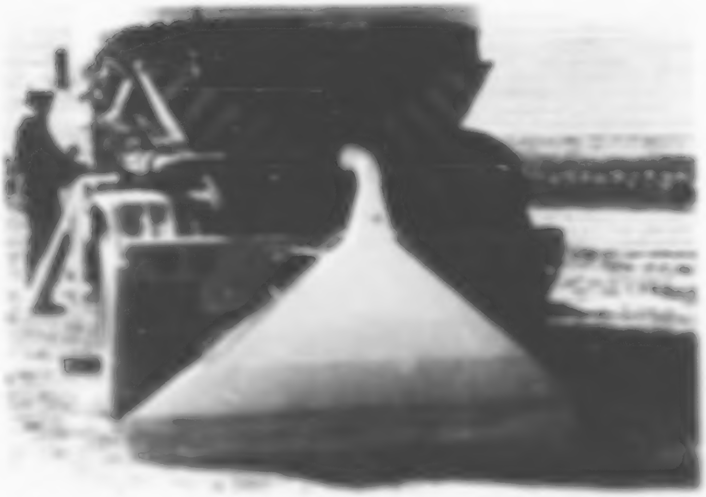


Figure 5. Air bottle transport truck equipped with a special distribution boot attached to the rear and an outrigger on the left.

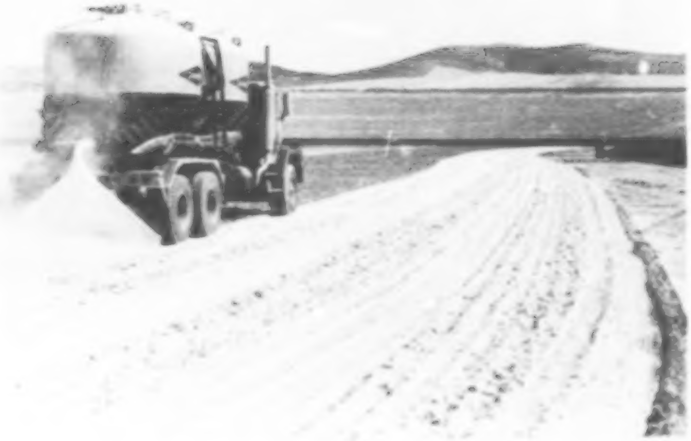


Figure 6. Application of modified bentonite soil sealant using an air bottle transport truck.

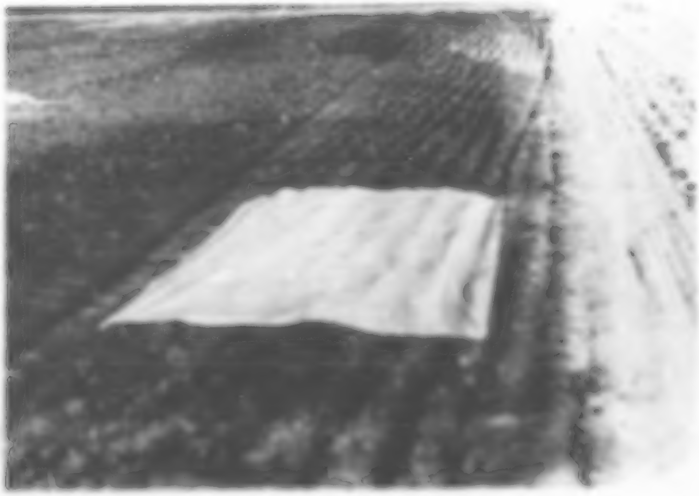


Figure 7. A piece of tarp is used to assure the proper quantity of soil sealant is applied to the soil.

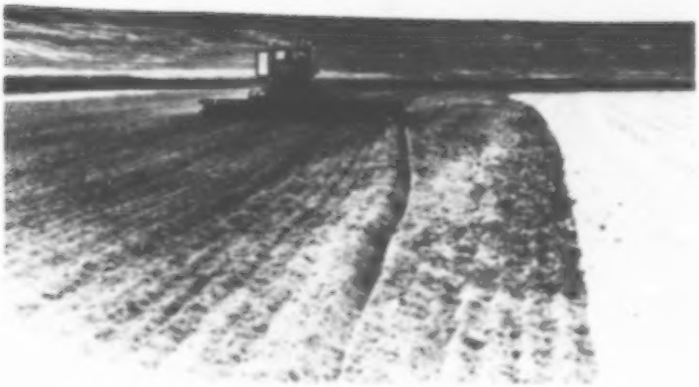


Figure 8. A disc is used to blend the modified bentonite into the soil.

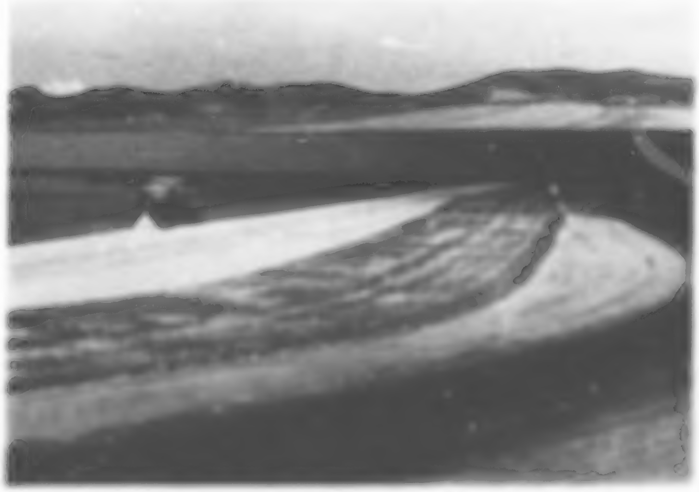


Figure 9. An overview of sealant application and blending activities.

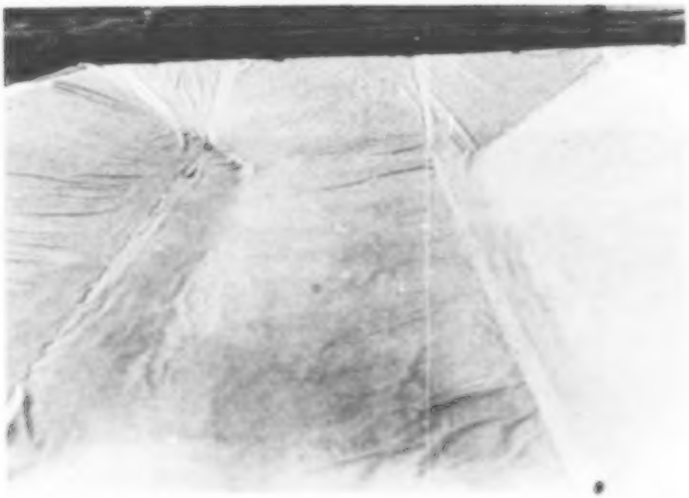


Figure 10. A fabric mat anchored in position which will be covered with a spray-on liner system.

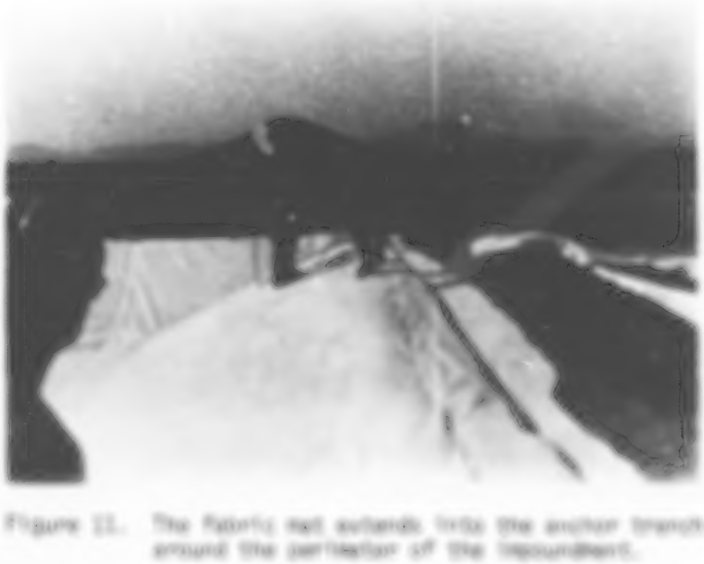


Figure 11. The fabric mat extends into the anchor trench around the perimeter of the impoundment.

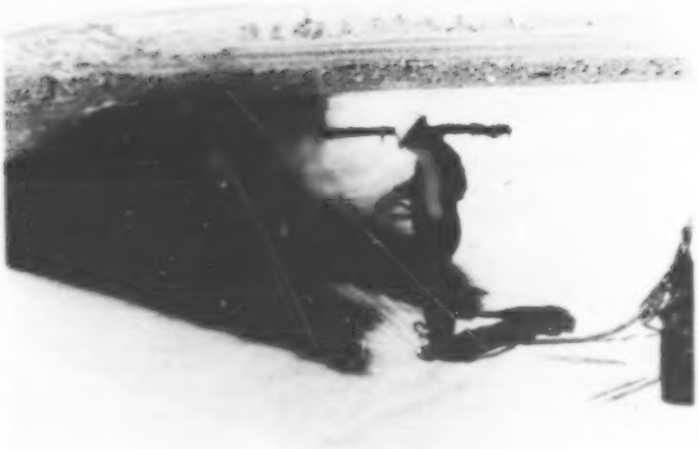


Figure 12. A workman applies a methane asphalt to a fabric mat usig a hand held spray applicator.

IDENTIFICATION OF HAZARDOUS WASTE FOR LAND TREATMENT RESEARCH

Joan B. Berkowitz, Judith C. Harris, and Bruce Goodwin
Arthur D. Little, Inc.
Cambridge, Massachusetts 02140

ABSTRACT

A methodology is discussed for identifying and prioritizing hazardous waste streams, potentially amenable to land treatment as a waste management option. The methodology is being developed to suggest promising candidates for land treatment research, field testing, and verification.

INTRODUCTION

Under contract to the U. S. Environmental Protection Agency, Cincinnati, Ohio, Arthur D. Little, Inc. is currently working on a project to identify potential industrial waste candidates for land treatment techniques. The objectives of the project are: (1) to identify and prioritize hazardous waste streams likely to be amenable to landtreatment as a management alternative and (2) to recommend laboratory and field research to fill in significant data gaps and to verify the environmental acceptability of landtreatment as a waste treatment/resource recovery method for a significant fraction of the hazardous wastes generated.

The scope of work includes:

- Development of prioritization criteria for ranking hazardous wastes potentially suitable for treatment and/or utilization in a land treatment facility;
- Application of the criteria to the list of wastes promulgated and proposed by the U.S. EPA to be regulated as hazardous under RCRA, Subtitle C;
- Identification of research requirements to verify the suitability of land treatment for the more promising hazardous waste streams;
- Recommendations for future research programs.

The RCRA regulations published in the Federal Register of May 19, 1980 (Vol. 45, No. 98, p. 33205 ff) define a land treatment facility as "that part of a facility at which hazardous waste is applied onto or incorporated into the soil surface." Land treatment practice generally involves application of waste to the soil surface, or injection of waste immediately below the surface, and incorporation of the waste into the upper 6-8 inches of the soil by standard farming techniques such as plow harrowing or disc burrowing. In contrast to hazardous waste landfills, which are designed for long term storage of wastes, land treatment facilities are designed to use the soil system for physical/chemical/biological treatment of hazardous waste constituents.

Land treatment has been used for oily wastes from the petroleum refining industry for more than 25 years. To our knowledge, none of these land treatment facilities, which are located in many different parts of the country, have given rise to human health or environmental damages incidents. Furthermore, extensive monitoring of field sites has demonstrated that certain types of oily wastes are transformed in an aerobic soil environment to a less hazardous or non-hazardous composition.

Land treatment is not used extensively

for hazardous wastes other than petroleum refining wastes, but the U.S. EPA has stated that it "may be feasible for other types of wastes" (Fed. Reg. Vol. 45, No. 98, May 19, 1980, p. 33205). In order to use land treatment for the management of a hazardous waste, one must demonstrate that the waste can be made less hazardous or non-hazardous by biological degradation or chemical reactions occurring in or on the soil. Demonstration of the feasibility of land treatment for any particular hazardous waste will generally involve a three step process. The first step consists of analysis of the waste, and review of available information on the biological and chemical action of natural soil treatment processes on each of the waste constituents in order to establish whether or not land treatment appears to be promising. The next step would involve laboratory and greenhouse studies under simulated field conditions to obtain basic data on degradability, sorption and mobility, volatilization, and toxicity, suitable for developing a preliminary land treatment facility design and operating plan. Finally, since water-soil interactions are difficult to predict, and not easily simulated in the laboratory, field pilot studies will generally be carried out to verify the feasibility and environmental acceptability of the preliminary design and operating plan. Each step requires an increased commitment of resources. Hence, it is important to develop decision criteria for proceeding from the initial assessment, to laboratory studies, and ultimately to field testing. The purpose of this paper is to suggest a highly simplified approach to deciding whether land treatment appears to be sufficiently promising for wastes listed as hazardous under RCRA to warrant laboratory testing and/or field demonstration.

METHODOLOGY

The approach being used to meet the objectives of the program is based on the Stage I land limiting constituent analysis proposed by Overcash.[illegible] This analysis focuses primarily on plant-soil assimilative capacity, and Overcash's "basic nondegradation constraint." The latter is stated by Overcash as follows:

> "The industrial waste, when considered on a constituent-by-constituent basis, shall be applied to the plant-soil system at such rates or over such limited time spans that no land is irreversibly removed from some other potential societal usage."

Since the present program is concerned with land treatment as a hazardous waste management option, the emphasis here is on soil assimilative capacity. Plants may not be grown, and generally will not be grown, on industrial hazardous waste land treatment sites. However, following closure, the site should conform to the basic nondegradation constraint.

For purposes of ranking wastes listed as hazardous under RCRA with respect to potential land treatment effectiveness, a series of three screens are being developed- (1) a heavy metal screen; (2) an organics screen; and (3) a screen for mobile conservative species. The data requirements for application of each screen include quantitative information on waste generation and composition, and general information on soil assimilative capacity for a wide range of hazardous waste constituents. The screening methodology is based on average annual rates of waste generation by individual manufacturers in each waste generating industry of interest. The average was calculated by dividing the annual rate of waste generation for the industry segment by the number of waste generating plants in the industry segment. It has been assumed that land treatment would be given low priority by a waste generator, if a land area greater than 100 acres (40 ha) would be required to assimilate the wastes from an individual plant for a period of 10 years. This figure is somewhat arbitrary, but does correspond to a relatively large soil-based waste management facility in current operating practice.

Assembly of Basic Data

For each waste listed as hazardous in the proposed RCRA regulations of December 18, 1978 (Fed. Reg. December 18, 1978, Vol. 43, No. 243), the following data were tabulated to the extent that they were available:

- Annual rate of waste generated (kg/yr) = [illegible]
- Number of waste generating plants = [illegible]

- Average rate of waste generation per plant (kg/yr/plant) = R/N;

- Waste composition (chemical components of the waste and the fraction of the waste accounted for by each chemical component);

- Annual rate of generation of each component in the waste stream from an average plant (kg/yr/plant).

The primary sources of data were the background documents prepared by the EPA to justify listing of the waste streams as hazardous; a series of EPA studies on hazardous waste management in a number of major waste generating industries(2)-(14) and other available published and unpublished literature.

Data on the composition of hazardous wastes is very limited, and has focused largely on major constituents and hazardous components. Available data only permit a very rough screening of listed wastes as primary potential candidates for land treatment research and demonstration. Chemical analyses are typically insufficient for a mass balance. Metals analyses are typically not available for waste streams that are primarily organic chemical in nature. For waste streams that are primarily inorganic in nature, analyses are often limited to toxic heavy metals, with little data on anionic constituents or other metals such as sodium, calcium, magnesium, etc. which also impact on land treatment feasibility.

Metals Screen

Based only on available metals analysis data for each waste stream, area requirements were calculated for assimilation of each analyzed metal, if all of the waste from an average plant were applied for a period of ten years. From this analysis, the land limiting constituent was identified (LLC), the constituent requiring the largest land area for assimilation. With the assumption that the soil pH would be maintained between 6 and 7.5, cumulative limits for metals are primarily a function of soil cation exchange capacity (CEC). Four prioritization categories for further research were defined as follows:

Prioritization Category	Area Requirement for LLC	CEC
High	≤ 40 ha	< 5
Moderately High	≤ 40 ha	5-15
Moderate	≤ 40 ha	> 15
Low	> 40 ha	< 15

The rationale for the first three categories is that if a site smaller than 100 acres will suffice in soil of low CEC, then soils of higher CEC will also be acceptable. Hence, there would be a wider choice of sites than if a CEC of 15 or more were required.

Allowable cumulative limits used in the analysis are given in Table 1.

TABLE 1. ALLOWABLE CUMULATIVE LIMITS (kg/ha)

	CEC		
Metal	<5	5 - 15	>15
Cd	5	10	20
Cu	125	250	500
Pb	500	1000	2000
Ni	50	100	200
Zn	250	500	1000

Other metals limits not available as a function CEC:

Mo 100 - 1000 kg/ha
Hg 8 - 10 kg/ha at [illegible] kg/ha/yr of 5
Be 2000 kg/ha
Tl very high
Sb <5000 kg/ha
Cr 500 kg/ha (10% estimate based on a similarity to lead)

Source: Reference (1).

Results are given in Table 2. In addition to the key information under the column headings "Area Required for Landtreatment" and "Prioritization Category," a column titled, "Excess Area Requirement Factor" gives the ratio of the total calculated land area requirement divided by 40 ha. The latter quantity provides a a rough measure of the extent to which a given waste stream exceeds the 40 ha nominal land use area constraint. With the single exception of "Lead Alkyl, Filter Liquor from Gasoline Additive Industry" waste, all inorganic waste streams were found to be unsuitable for landtreatment using this approach due to high concentra-

Table 2. Heavy Metals Screen of Hazardous Waste Streams for Land Treatment Suitability

Listed Waste Stream		Heavy Metal	Average Quantity Generated per Plant (kg/10 yrs)	Area Required for Land Treatment (ha)	Prioritization Category	Excess Area Requirement Factor	Comments
Primary Copper Smelting and Refining - Blowdown Slurry/Sludge	Acid Plant	Cd	3.9x10^{4} kg	7.8x10^{3}(C.E.C. <5) 3.9x10^{3}(C.E.C. 5-15) 2.0x10^{3}(C.E.C. >15)	low low low	2.0x10^{2} 98 50	Cd and Cr concentrations in leachpit given in background document, but no annual volume given
		Pb	6.0x10^{5} kg	1.2x10^{3}(C.E.C. <5) 6.0x10^{2}(C.E.C. 5-15) 3.0x10^{2}(C.E.C. >15)	high	30 15 7.5	
		Hg	60 kg	7.5-6.0	high	--	Quantity generated based on amount disposed; remainder is recycled
		Cr	3.8x10^{3} kg	7.6-1.0	high	--	
		Se	2.3x10^{3} kg	?		?	
Primary Lead Smelting - Dredged Solids from Liquid Waste Impoundments	Plant A	Cd	1.5x10^{4} kg	3.0x10^{3}(C.E.C. <5) 1.5x10^{3}(C.E.C. 5-15) 7.5x10^{2}(C.E.C. >15)	low mod.high moderate	75 38 19	Concentration and generation rates for both Cd and Pb given in backbackground document, but the numbers do not agree; generation rates (kg/yr) given in background document were used for this calculation.
		Pb	2.9x10^{5} kg	5.8x10^{2}(C.E.C. <5) 2.9x10^{2}(C.E.C. 5-15) 1.5x10^{2}(C.E.C. >15)	high	15 7.3 3.8	
	Plant B	Cd	5.6x10^{4} kg	1.1x10^{4}(C.E.C. <5) 5.6x10^{3}(C.E.C. 5-15) 2.8x10^{3}(C.E.C. >15)	low low low	2.8x10^{2} 1.4x10^{2} 70	Concentration data given in background document may not apply to waste from plants for which generation rates are given.
		Pb	8.2x10^{4} kg	5.8x10^{2}(C.E.C. <5) 2.9x10^{2}(C.E.C. 5-15) 1.5x10^{2}(C.E.C. >15)	low low low	15 7.3 3.8	
Secondary Lead Smelting - Emission Control Dusts/Sludges	Sludges	Pb	6.8x10^{10}-7.6x10^{10} kg	1.4-1.5x10^{8}(G.E.C. <5) 6.8-7.6x10^{7}(C.E.C. 5-15) 3.4-3.8x10^{7}(C.E.C. >15)	low low low	3.8x10^{6} 1.9x10^{6} 9.5x10^{5}	
		Cd	4.4x10^{8}-4.9x10^{8} kg	8.8-9.8x10^{7} (C.E.C. <5) 4.4-4.9x10^{7} (C.E.C. 5-15) 2.2-2.5x10^{7} (C.E.C >15)	low low low	2.5x10^{5} 1.2x10^{5} 6.3x10^{5}	
		Cr	3.8x10^{4}-4.3x10^{7} kg	(7.6-8.6x10^{4}) - (9.5x10^{3}-1.1x10^{4})	low	2.2x10^{3}	1980 estimate for total quantity of waste generated was used for this calculation.
	Dusts	Pb	9.2x10^{9}-1.0x10^{10} kg	1.8-20x10^{7}(C.E.C. <5) 9.2x10^{6}-1.0x10^{7}(C.E.C.5-15) 4.6-5.0x10^{6}(C.E.C.>15)	low low low	5.0x10^{5} 2.5x10^{5} 1.3x10^{5}	

Heavy Metals Screen of Hazardous Waste Streams for Land Treatment Suitability (continued)

Listed Waste Stream		Heavy Metal	Average Quantity Generated per Plant (kg/10 yrs)	Area Required for Land Treatment (ha)	Prioritization Category	Excess Area Requirements Factor	Comments
Secondary Lead Smelting - Emission Control Dusts/ Sludges (continued)	Dusts (cont'd)	Cd	$6.9 \times 10^7 - 7.7 \times 10^7$ kg	$1.4-1.5 \times 10^7$(C.E.C. <5) $6.9-7.7 \times 10^6$(C.E.C. 5-15) $3.5-3.9 \times 10^6$(C.E.C. >15)	low low low	3.8×10^5 1.9×10^5 9.5×10^4	
		Cr	$1.1 \times 10^7 - 1.3 \times 10^7$ kg	$(2.2-2.6 \times 10^4)-$ $(2.8-3.3 \times 10^3)$	low	83	
Spent Pickle Liquors from Steel Finishing Industry and Treatment Sludge	Sludges	Pb	2.4×10^6 kg	4.8×10^3(C.E.C. <5) 2.4×10^3(C.E.C. 5-15) 1.2×10^3(C.E.C. >15)	low low low	1.2×10^2 60 30	
		Cr	4.7×10^6 kg	$9.4-1.2 \times 10^3$	low	2.4×10^2	
	H_2SO_4 liquor	Cr	$2.1 \times 10^3 - 2.1 \times 10^4$ kg	(4.2-42)-(.53-5.3)	high	1.1	Concns. and volume generation rates given in background document for 3 acid waste streams; distribution of those streams assumed to be the same among all 240 plants.
		Pb	$0-1.6 \times 10^2$ kg	3.2×10^{-1}(C.E.C. <5) 1.6×10^{-1}(C.E.C. 5-15) 8.0×10^{-2}(C.E.C. >15)	high	none	
	HCl liquor	Cr	$2.5 \times 10^2 - 4.6 \times 10^3$ kg	(0.5-9.2)-(.06-1.2)	high	none	
		Pb	$2.5 \times 10^2 - 1.9 \times 10^5$ kg	$5.0 \times 10^{-1} - 3.8 \times 10^2$ $2.5 \times 10^{-1} - 1.9 \times 10^2$ $1.3 \times 10^{-2} - 95$	low-high low-mod.high low-moderate	9.5 4.8 2.4	
	Mixed acids	Cr	$3.9 \times 10^4 - 5.0 \times 10^4$ kg	(78-100)-9.8-13)	low-high	2.5	
		Pb	11-47 kg	$2.2 \times 10^{-2} - 9.4 \times 10^{-2}$ $1.1 \times 10^{-2} - 4.7 \times 10^{-2}$ $5.5 \times 10^{-3} - 2.4 \times 10^{-2}$	high	none	
Electric Furnace Production of Steel--Emission Control Dusts/Sludges	Dust	Mn	3.8×10^6 kg	$7.6-3.8 \times 10^3$	low	1.9×10^2	Number of plants and component generation rates calculated from data in background documentation total U.S. steel production, average plant capacity, and amount of waste/unit volume of product.
		Ni	3.5×10^5 kg	7.0×10^3(C.E.C. <5) 3.5×10^3(C.E.C. 5-15) 1.8×10^3(C.E.C. >15)	low low low	1.8×10^2 88 45	
		Pb	$8.3 \times 10^4 - 1.4 \times 10^6$ kg	$1.7 \times 10^2 - 2.8 \times 10^3$(C.E.C. <5) $83-1.4 \times 10^3$(C.E.C. 5-15) $42-7.0 \times 10^2$(C.E.C. >5)	low low low	70 35 18	
		Cr	1.1×10^6 kg	$2.2 \times 10^3 - 2.8 \times 10^2$	low	55	Concentrations of Pb and Cr in leachate given in background document, but no corresponding annual generation rate.

Heavy Metals Screen of Hazardous Waste Streams for Land Treatment Suitability (continued)

Listed Waste Stream		Heavy Metal	Average Quantity Generated per Plant (kg/10 yrs)	Area Required for Land Treatment (ha)	Prioritization Category	Excess Area Requirements Factor	Comments
Electric furnace production of steel--emission control dusts/sludges	Dust (cont'd)	Zn	$2.3x10^5$ kg	$9.2x10^2$(C.E.C. <5) $4.6x10^2$(C.E.C. 5-15) $2.3x10^2$(C.E.C. >15)	low low low	23 12 5.8	
		Cu	$5.7x10^4$ kg	$4.6x10^2$(C.E.C. <5) $2.3x10^2$(C.E.C. 5-15) $1.1x10^2$(C.E.C. >15)	low low low	12 5.8 2.8	
	Sludge	Pb	$2.4x10^4$ kg	48 (C.E.C. <5) 24 (C.E.C. 5-15) 12 (C.E.C. >15)	low mod. high	1.2 none	
		Cr	$8.1x10^3$ kg	16-2	high	none	
Primary zinc smelting and refining - Process wastewater treatment sludge and/or acid blowdown	Anode Slimes/ Sludges	Pb	$2.1x10^6$-$4.0x10^6$ kg	4.2-$8.0x10^3$(C.E.C. <5) 2.1-$4.0x10^3$(C.E.C. 5-15) 1.1-$2.0x10^3$(C.E.C. >15)	low low low		Total annual quantities anode slimes/sludges and cadmium plant residues used for this calculation, since number of plants generating these kinds of wastes is not clear from background document; number of plants would have to be ≥50 for anode slimes/sludges and ≥5 for cadmium plant residues to satisfy per plant area constraint (i.e., ha) for land treatment suitability.
		Cd	280-$3.3x10^4$ kg	56-$6.6x10^3$(C.E.C. <5) 28-$3.3x10^3$(C.E.C. 5-15) 14-$1.7x10^3$(C.E.C. >15)	low low low		
	Cadmium plant residues	Pb	$3.9x10^5$ kg	$7.8x10^2$(C.E.C. <5) $3.9x10^2$(C.E.C. 5-15) $2.0x10^2$(C.E.C. >15)	low low low		
		Cd	$5.1x10^2$ kg	$1.0x10^2$(C.E.C. <5) 51 (C.E.C. 5-15) 26 (C.E.C. >15)	low low moderate		
Primary zinc smelting and refining process wastewater treatment sludge and/or acid blowdown	Pyrometallurgical process acid plant blowdown sludge-Plant A	Cd	$5.7x10^4$-$1.9x10^5$ kg	1.1-$3.6x10^4$(C.E.C. <5) $5.7x10^3$-$1.8x10^4$(C.E.C.5-15) 2/$0x10^3$-$9.0x10^3$(C.E.C.>15)	low low low	$9.0x10^2$ $4.5x10^2$ $2.3x10^2$	Total quantity of acid plant blowdown sludge and to contribution of 2 plants to total quantity given in background document used for this calculation; proportion of total quantity of waste accounted for by lime treatment sludges and electrolyte process acid plant blowdown sludges not clear from background document and assumed for purposes of this calculation to be ≈0.
		Pb	$3.8x10^5$ kg	$7.6x10^2$(C.E.C. <5) $3.8x10^2$(C.E.C. 5-15) $1.9x10^2$(C.E.C. >15)	low low low	19 9.5 4.8	
	Pyrometallurgical process acid plant blowdown sludge-Plant B	Cd	$1.3x10^3$-$4.0x10^3$ kg	2.6-$8.0x10^2$(C.E.C. <5) 1.3-$4.0x10^2$(C.E.C. 5-15) 65-$2.0x10^2$(C.E.C. >15)	low low low	20 10 5	
		Pb	$8.6x10^3$ kg	19 (C.E.C. <5) 8.6 (C.E.C. 5-15) 4.3 (C.E.C. >15)	high	none	

Heavy Metals Screen of Hazardous Waste Streams for Land Treatment Suitability (continued)

Listed Waste Stream		Heavy Metal	Average Quantity Generated per Plant (kg/10 yrs)	Area Required for Land Treatment (ha)	Prioritization Category	Excess Area Requirements Factor	Comments
Electroplating and metal finishing operations--wastewater treatment sludge		Cr, Cd, Ni	?				No data for quantity of waste generated.
Wastewater treatment sludge from production of pigments	Chrome yellow and orange	Cr	$1.3x10^4-1.6x10^4$ kg	(260-320)-(33-40)	low-high	none	
		Pb	$4.5x10^5-5.6x10^5$ kg	$9.0x10^2-1.1x10^3$	low	28	Quantity of waste generated given in background document is for entire chromium pigment industry
				$4.5-5.6x10^2$	low	14	
				$2.3-2.8x10^2$	low	7	
	Molybdate orange	Pb	$3.0x10^5-3.7x10^5$ kg	$6.0-7.4x10^2$	low	19	
				$3.0-3.7x10^2$	low	9.3	
				$1.5-1.9x10^2$	low	4.7	
		Cr	$1.1x10^4-1.3x10^4$ kg	(260-320)-(33-40)	high	none	
	Zinc yellow	Zn	$1.3x10^5-1.6x10^5$ kg	$5.2-6.4x10^2$(C.E.C. <5)	low	16	
				$2.6-3.2x10^2$(C.E.C. 5-15)	low	8	
				$1.3-1.6x10^2$(C.E.C. >15)	low	4	
		Cr	$2.3x10^5-11.4x10^5$ kg	$1.3x10^3-1.6x10^3$	low	40	
				$1.6x10^2$ -2.0x102	low	5.0	
	Chrome green	Pb	$3.6x10^4-4.4x10^4$ kg	72-88	low	2.2	
				36-44	mod.high-low	1.1	
				18-22	moderate	none	
		Cr	$9.0x10^3-1.1x10^4$ kg	(18-22) - (2-28)	high	none	
	Chrome oxide green	Cr	$2.3x10^5-2.9x10^5$ kg	$(1.3x10^3-1.6x10^3)$ - (70-73)	low	40	
Oven residue from production of chrome oxide green pigments		Cr	$1.2x10^5-1.4x10^5$ kg	$(2.4-2.8x10^2)$ - (30-35)	low	7	Quantity of waste generated given in background documents is for entire chromium pigment industry

tions or large total amounts of one or more waste constituents. Inspection of the "Excess Area Requirement Factors" column shows that for most wastes the calculated land area requirements are substantially in excess of our 40 ha maximum criterion, with factors ranging from one to several orders of magnitude. Had these factors been on the order of 2 - 3 or less, we may reasonably have concluded that waste pretreatment or other pre-waste application alternatives could be considered which might improve the landtreatment potential for certain wastes. Given the large volumes of most waste streams and the substantial amount of pretreatment that would apparently be required, these alternatives do not appear to be economically justifiable and have not been considered further.

Organics Screen

Over 70 organic compounds have been identified as major constituents among the waste streams listed as hazardous by the EPA. The most important criterion for the potential effectiveness of land treatment for organic chemical wastes is environmental persistence. For screening purposes, waste streams that contain one or more constituents with half-lives in soil of more than nine months were considered of low priority for future research. The nine-month cut-off point was derived as the half-life necessary to rid a landtreatment area of 99.99% of its waste application in 10 years so that applications in year one would be degraded by the beginning of a 20-year post-closure period. Waste streams are scored for persistence as follows:

Priority for Research	Half-Life in Soil
High	less than 7 days
Moderately high	1 - 4 weeks
Moderate	1 - 5 months
Moderately low	5 - 9 months
Low	greater than 9 months

Persistence ratings for a number of hazardous waste constituents are given in Table 3. These were derived from published biodegradation data including half-lives, hydrolysis, photolysis and biodegradation rate constants, Tabak static culture flask numbers, BOD_5 data and BOD/COD ratios.

TABLE 3. PERSISTENCE OF ORGANIC HAZARDOUS WASTE CONSTITUENTS IN SOIL

Organic Component	Persistence
Acetonitrile	H
Acrolein	H
Acrylamide	H
Acrylonitrile	MH
Benzal chloride	H
Benzanthracene	L
Benzofluoranthene	L
Benzopyrene	L
Benzotrichloride	H
Benzyl chloride	H
Carbon tetrachloride	L
Chlordane	L
Chloroacetaldehyde	M
Chlorobenzene	H
Chloroethers	H
Chloroform	MH
Creosote	H
Dichloroethane	M
o-Dichlorobenzene	H
2,4-Dichlorophenol	H
2,6-Dichlorophenol	H
Dichloropropanol	H
m-Dinitrobenzene	M
2,4-Dinitrotoluene	M
Epichlorohydrin	H
Ethylchloride	MH
Formaldehyde	MH
Formic acid	H
Heptachlor	L
Hexachlorobenzene	L
Hexachlorobutadiene	MH
Hexachlorocyclopentadiene	MH
Hexachloroethane	ML
Hydrocyanic acid	L
Maleic anhydride	H
Methylchloride	MH
Methylene chloride	MH
Napthaquinones	H
Nitrobenzene	M
Paraldehyde	M
Phenol	MH
Phorate	M
Phosphorodithioic acid	M
Phosphorodithioic esters	M
Phosphorothioic exters	M

TABLE 3. PERSISTENCE OF ORGANIC HAZARDOUS WASTE CONSTITUENTS IN SOIL (concluded)

Organic Components	Persistence
Picoline	H
Phythalic anhydride	M
Pyridine	H
Quinones	H
Tetrachloroethanes	L
Tetrachloroethylene	MH
Toluene	H
Toluene diamines	MH
Toluene diisocyanates	H
Toxaphene	L
Trichloroethanes	L
Trichloroethylene	H
o,o,o-Triethyle ester, Phosphorodithioic acid	M
2,4,6-Trichlorophenol	MH
Trichloropropane	H
Vinyl chloride	H
Vinylidene chloride	MH

The persistency rating of a waste stream was assigned a low value if any constituent with a half-life greater than nine months was present. Streams that do not contain constituents with t1/2 greater than 9 months receive a persistence score obtained by weighted averaging the persistence scores of all the stream constituents.

REFERENCES

1. Battelle-Columbus Laboratories, "Assessment of Industrial Hazardous Waste Practices: Electroplating and Metal Finishing Industries--Job Shops," U.S. Environmental Protection Agency, in preparation, to be distributed by the National Technical Information Service.
2. WAPORA, Inc., "Assessment of Industrial Hazardous Waste Practices: Paint and Allied Products Industry Contact Solvent Reclaiming Operations, and Factory Application of Coatings," Environmental Protection Publication SW-119c, U.S. Environmental Protection Agency, PB-251 669 (1976).
3. WAPORA, Inc., "Assessment of Industrial Hazardous Waste Practices--Special Machines Manufacturing Industries," U.S. Environmental Protection Agency, in preparation, to be distributed by the National Technical Information Service.
4. Jacobs Engineering Company, "Assessment of Industrial Hazardous Waste Practices in the Petroleum Refining Industry," U.S. Environmental Protection Agency, in preparation, to be distributed by the National Technical Information Service.
5. Gruber, G. I., "Assessment of Industrial Hazardous Waste Practices, Organic Chemicals, Pesticides, and Explosives Industries," Environmental Protection Publication SW-118c, U.S. Environmental Protection Agency, PB-251 307 (April 1975).
6. Versar, Incorporated, "Assessment of Industrial Hazardous Waste Practices, Storage and Primary Batteries Industries," Environmental Protection Agency, PB-241 204 (January 1975).
7. Calspan Corporation, "Assessment of Industrial Hazardous Waste Practices in the Metal Smelting and Refining Industry," U.S. Environmental Protection Agency, in preparation, to be distributed by the National Technical Information Service.
8. Versar, Incorporated, "Assessment of Industrial Hazardous Waste Practices, Textiles Industry," U.S. Environmental Protection Agency, in preparation, to be distributed by the National Technical Information Service.
9. Foster D. Snell, Inc., "Assessment of Industrial Hazardous Waste Practices, Rubber and Plastics Industry," U.S. Environmental Protection Agency, in preparation, to be distributed by the National Technical Information Service.
10. Shaver, R. G., et al., "Assessment of Industrial Hazardous Waste Practices: Inorganic Chemicals Industry," Environmental Protection Publication SW-104c, U.S. Environmental Protection Agency PB-244 832 (March 1975).

11. SCS Engineers, Inc., "Assessment of Industrial Hazardous Waste Practices--Leather Tanning and Finishing Industry," U.S. Environmental Protection Agency, in preparation, to be distributed by the National Technical Information Service.

12. Arthur D. Little, Inc., "Pharmaceutical Industry: Hazardous Waste Generation, Treatment, and Disposal," Environmental Protection Publication SW-508, U.S. Environmental Protection Agency, 1976.

13. Swain, John W., Jr., "Assessment of Industrial Hazardous Waste Management Practices: Petroleum Rerefining Industry," U.S. Environmental Protection Agency, in preparation, to be distributed by the National Technical Information Service.

14. WAPORA, Inc., "Assessment of Industrial Hazardous Waste Practices--Electronic Components Manufacturing Industry," U.S. Environmental Protection Agency, in preparation, to be distributed by the National Technical Information Service.

STATISTICAL ANALYSIS OF TRACE METAL CONCENTRATIONS IN SOILS AT SELECTED LAND TREATMENT SITES

Michael A. Grossman
Bruce A. Goodwin
Paul M. Brenner
Arthur D. Little, Inc.
Cambridge, Massachusetts 02140

ABSTRACT

The problem of determining the sample size necessary to determine if a significant increase in trace metal concentrations in waste application area soils relative to control area soils has occurred is addressed. The paper discusses the sampling of two land treatment sites, sampling plans, and hypothesis testing and sample size considerations. The use of statistical techniques are demonstrated using data obtained from the sampling and chemical analysis of soils from the two land treatment sites. The two sample t-test is recommended as the most appropriate statistical test. Setting the minimum significant difference equal to the sample standard deviation is shown to yield a useful criterion for determining the necessary number of soil samples. A modification of two stage sampling to the periodic sampling of land treatment sites is also recommended.

INTRODUCTION

The goal of the analysis presented in this paper is to determine if the concentration of specific chemicals in the soil has changed significantly from background levels at land treatment sites. Geological, chemical and statistical analysis all play an important role in determing if a change has occurred. Geological analysis must determine the homogeneity of the soil conditions and how well each soil sample represents the surrounding land area. Chemical analysis of the soil samples must measure the concentration of the chemicals of interest precisely and determine the tolerance limits of these measurements. The statistical analysis must determine if a significant change has occurred based on the data provided by the prior two analyses. This paper discusses the sampling of two land treatment sites, sampling plans, and hypothesis testing and sample size considerations. The use of statistical techniques are demonstrated using data obtained from the sampling of the two land treatment sites. Conclusions and recommendations are made.

FIELD SAMPLING OF TWO LAND TREATMENT SITES

Two active industrial land treatment operations were studied. The minimum criteria for site selection were that the sites should have identifiable and appropriate control and waste application areas, and that the wastes should be representative of the range of waste compositions encountered in actual practice. Control areas had to be at least one acre in area to permit collection of the desired minimum number of samples for statistical analysis. Otherwise, they were as nearly identical as possible to the waste application areas except that no waste had been applied.

The same minimum area requirement was applied to waste application areas. In addition, reasonably accurate descriptions of the types and amounts of wastes applied were obtained from personnel familiar with the site to assure that the area had not been subject to other activities which might influence the analysis. Candidate waste types were not limited to wastes which could be classified as hazardous according to proposed federal regulations, since we wished to test the hypothesis that assessment of the variability of waste constituent concentrations does not necessarily require measurement of a particular species. Rather, information was obtained on a group of chemical characteristics which included species which were of particular interest because they were considered likely to serve as indicators of waste constituent accumulation and/or migration.

The sites actually chosen for this study satisfied all these criteria. Site A was a plastics manufacturing facility which landfarmed a centrifuged sludge from an activated sludge wastewater treatment system. The waste is known on the basis of chemical analysis to contain percentage concentrations of sodium. Waste composition was reported to be relatively constant over time. Waste was applied by subsurface injection and mixed further with the soil by ordinary farm cultivation methods. Site B was a petroleum refinery which landfarmed sludge collected from wastewater holding ponds. Considerable variation in the composition of the waste over time was considered likely by site personnel. Chemical analysis of selected waste samples indicated the percentage concentrations of chromium were typically present in the landfarmed material. Waste was applied by gravity flow from vacuum transport trucks and mixed further with the soil by tractor-drawn rototiller.

Soil and core samples were collected from both an application and a control area and from two depths:

Depth 1: 0- 6 inches below grade
Depth 2: 6-12 inches below grade

At Site A, the control area had 20 equally spaced sampling locations taken approximately 45 feet apart from one acre; and the application area had 60 sampling locations taken approximately 45 feet apart from three acres. At Site B, 20 equally spaced soil samples were taken from both the application and control areas. Sampling locations were approximately 45 feet apart on one acre sampling areas. The patterns of the sampling site locations for each area were:

1. A triangular pattern for the control area of Site A;
2. A rectangular pattern for the three other areas sampled.

A total of 240 soil core samples collected from Sites A and B were analyzed and results for the following seven constituents are reported later in the paper:

1. Chromium
2. Copper
3. Lead
4. Nickel
5. Sodium
6. Zinc
7. Conductivity

The six metals--chromium, copper, lead, nickel, sodium, and zinc--were determined in nitric-perchloric acid digests of all soil samples using plasma emission spectroscopy. Conductivity was determined in a 1:1 soil-water extract using a portable conductivity meter. Conductivities are reported in units of micromhos per centimeter. All other results are expressed as parts per million in air-dry soil.

The results of all chemical analyses and statistical calculations are available from the authors upon request.

SAMPLING PLANS

In each land treatment site, there are two areas of interest to be sampled: the application (treatment) area and the control area. The object of the sampling plan is to furnish soil samples representative of each area in sufficient number to determine if a significant difference in concentration between the two areas exists. Several operations will be discussed and some suggestions made for selecting from among the sampling plans.

It is most important to remember that the sampling plans and sample sizes discussed in this paper apply to each area (application and control) of a land treatment site. They are not designed for any arbitrary land areas such as an acre. As such, the land area they apply to is assumed to be uniform in its geological and chemical properties. If this assumption is violated, the plan must be revised to provide a separate set of soil samples for each homogeneous sub-area within the application and control areas. It is important to note that as long as geological and chemical judgements show the soil conditions to be uniform (homogeneous), the number of soil samples required will be a function of the statistical and chemical concentrations independent of the size of the area studied; i.e., the number of soil samples for a homogeneous area is not a function of land size (area).

A large number of standard statistical sampling techniques exist for selecting the soil samples. A few of the most common will be discussed briefly. Any statistically sound sampling plan which produces an accurate estimate of chemical concentrations in the soil within the required tolerances is valid.

Three of the most common plans which are almost exclusively used in sampling are:

1. Random Sampling - Sample sites are selected from the area of interest with equal probability. No stratifications or subareas are created.
2. Systematic Sampling - If n soil samples are needed from an area, the area is uniformly subdivided and n equally spaced soil samples are taken. This corresponds to subdividing the area into n subareas and taking one sample per subarea. The size of the subarea would be that of the total area divided by n. Systematic sampling is generally used for its ease and facility of choosing sample members when its use is appropriate.
3. Stratified Random and Stratified Systematic Sampling - Two or more subareas or strata are defined for an area to be sampled. Within each stratum the sample members are then selected randomly if stratified systematic sampling is used.

Most soil sampling has been performed as a single-stage sample. That is, all the soil samples are taken at one time or within a short period of time. A second method that may be advantageous when the chemical concentrations and their variances are unknown is two-stage sampling. With this method, the sampling is conducted in two parts. In the first stage a small pilot study is conducted to obtain estimates of the means and variances of the chemicals of interest. Then, when a clear idea of the sample size is known, a second, larger, full-scale sample is conducted based on revisions from the first stage. The results of both stages are pooled together for the analysis.

A pilot study is useful when the mean and variance of the quantity being measured is unknown. With estimates from the pilot study, a precise calculation of the sample size can be attempted. Furthermore, a pilot test gives the sampler a chance to test out his sampling methods and make any changes necessary to improve the ease and efficiency of his sampling.

HYPOTHESIS TESTING AND SAMPLE SIZE CONSIDERATIONS

After a sampling method has been chosen and the results of the pilot study analyzed, the next step in sampling is to determine the efficient (proper) sample size. To answer this question, it is necessary to study the relationship of the sample size to the hypothesis being tested and to decide (specify) the desired certainty of the answer. In the land treatment site monitoring context, the hypothesis tested by the monitoring program is: the concentrations of the chemical species in the soil are the same in the application and control areas, against the alternative that they are unequal. We wish to have the probability of reaching the wrong conclusion about our hypothesis or its alternative to be very small. The probability of incorrectly determining that the chemical concentrations of the two areas are unequal is denoted by the α-level; and the probability of incorrectly determining that the chemical concentrations are equal is denoted by the β-level. The first kind of error is known as Type I Error and the second as Type II Error. If we denote our hypothesis by H_0 and the alternative by H_1, Table 1 depicts the possibilities of the outcome of the analysis.

In choosing the sample size. protection against both Type I and Type II Error is sought. A common trap that must be avoided is committing a Type II Error when no difference between application and control areas has been found. This can occur when too small a sample size has been chosen; i.e., the sample size is too small to show the significant difference that does exist. In committing a Type II Error because of a small sample size, the experi-

TABLE 1. POSSIBLE OUTCOMES OF STATISTICAL ANALYSIS

	True Situation	
Conclusion of Analysis	H_0 True H_1 False	H_0 False H_1 True
H_0 True H_1 False	Conclusion Correct	Conclusion False (Type II Error)
H_0 False H_1 True	Conclusion False (Type I Error)	Conclusion Correct

menter observes no significant difference between application and control areas and, therefore, concludes that the chemical concentrations in the two soils are equal although the probability of that conclusion being incorrect is quite large.

In choosing the α and β levels, one would wish them to be very small. Typically, the α-level, the probability of committing a Type I Error (concluding the two areas are different when, in fact, they are the same) is chosen to be .05. One would want the same level of protection against the probability of committing a Type II Error (concluding the two areas are the same when, in fact, they are different) and it is reasonable to also set the β-level equal to .05. These α and β levels offer the experimenter adequate protection against error without being overly restrictive.

The next step in choosing the sample size is to inspect the statistical test used to differentiate between the two areas and observe what other quantities must be specified or estimated from the data. Since two areas are being compared for their chemical concentrations in soil, the statistical test used should be the two-sample t-test.

The test statistic for the t-test is:

$$\frac{\overline{X}_A - \overline{X}_C}{\sqrt{\dfrac{S_A2}{n_A} + \dfrac{S_C2}{n_C}}} \qquad (1)$$

where: $\overline{X}_A$ = average concentration for the application area

$\overline{X}_C$ = average concentration for the control area

S_A2 = the variance of the concentration in the application area

S_C2 = the variance of the concentration in the control area

n_A = the number of soil samples from the application area

n_C = the number of soil samples from the control area

The problem at hand is to determine n_A and n_C. The variances S_A2 and S_C2 are calculated (estimated from the sample data as are $\overline{X}_A$ and $\overline{X}_C$).

The last parameter that must be specified before the final sample size can be determined is the minimum difference between $\overline{X}_A$ and $\overline{X}_C$ which is to be considered significant. In other words, how small a difference between the chemical concentrations in each area do we wish to be able to detect? This is the margin the analyst wishes to be protected against for both Type I and Type II Errors. If the minimum difference between $\overline{X}_A$ and $\overline{X}_C$ is specified, the sample size for each homogeneous area can be estimated using the formula:

$$n = \left(U_{1-\beta} + U_{1-\alpha/2}\right)^2 \left(\frac{\sigma}{\overline{X}_A - \overline{X}_C}\right)^2 \qquad (2)$$

where $U_{1-\beta}$ and $U_{1-\alpha/2}$ are the standard normal deviates* for the indicated probability levels and σ is the standard deviation. If σ is unknown it may be estimated from the sample data.

Once the α and β levels have been specified, the sample size is a function of the right-hand factor in equation (2), i.e., $\left(\frac{\sigma}{\overline{X}_A - \overline{X}_C}\right)^2$. If this difference is denoted by d, where d = $\overline{X}_A - \overline{X}_C$, the sample size n is now seen as a function of the ratio σ/d. Since we are dealing with variances and means that are not known before the sampling is conducted, it is simpler and more sensible to state the minimum difference we wish to be able to detect as a percentage of the standard deviation, σ.

Once the minimum detectable difference is stated in terms of a percentage of the standard deviation, the σ/d ratio is defined and the sample size is a straightforward calculation.

For example, suppose one wanted to be able to detect a difference equal to one standard deviation. The α and β levels have already been specified as .05, so the probability of committing a Type I or Type II Error is set at .05. Then, the sample size is found to be:

$$\begin{aligned} n &\simeq \left(U_{1-\beta} + U_{1-\alpha/2}\right)^2 \left(\frac{\sigma}{d}\right)^2 \\ &\simeq (1.645 + 1.96)^2 \quad (1)^2 \\ &= 12.99 \end{aligned}$$

Therefore, the sample size, n, is rounded up to the nearest integer and is chosen to be 13. Similarly, if one wanted to be able to detect a difference equal to half of the standard deviation, the sample size would be four times greater or 52. One easily sees that overly restrictive specifications of the σ/d ratio can lead to huge sample sizes. If one wants to detect a very small difference and σ is large relative to d, then a large number of soil samples will be required.

Common sense should be used in specifying the σ/d ratio desired or d if an estimate of σ is known apriori, as from a pilot test. For example, if one wishes to set d equal to the chemical detection limit (which is quite small), while a relatively high concentration of the chemical is present in the soil and the variance is large, then astronomical sample sizes will be necessary to detect minute differences. Data from the two land treatment sites discussed in the next section will be used to illustrate the point.

The estimated detection limit for chromium is 0.5 ppm. The estimated average concentration of chromium at Site B was 264.65 ppm and the estimated standard deviation was 334.63. Substituting these values into the sample size formula with α and β set to .05 yields a necessary sample size in excess of 6.9 million soil samples per homogeneous area. In addition to being impractical, it is unnecessary to be interested in a difference of .5 ppm when the average is over 250 ppm. As a matter of fact, a highly significant difference between application and control area was demonstrated with 20 soil samples per area. A more sensible formulation would be to express the minimum observable difference as a percentage of the mean or in terms of the mean to standard deviation ratio.

For example, we might want the minimum detectable difference to be 10% of the control area mean. This assumes that estimates of the variance and application and control area mean exists. Another specification might be for the σ/d variance to minimum significant difference ratio to be specified as one or one-half. The decision to specify the sample size in either of the above two ways does not exempt the chemist and the geologist from telling the statistician how large a difference is significant in physical terms.

Table 2 lists and Figure 1 displays the sample size, n, as a function of the σ/d ratio for three combinations of protection from Type I and Type II Error (α and β levels):

1. $\alpha = \beta = .05$ (the suggested specifications)
2. $\alpha = \beta = .01$
3. $\alpha = .05$; $\beta = .10$

---

*Values from the Normal Probability Tables. For example, $U_{.975} = 1.96$ and $U_{.95} = 1.645$.

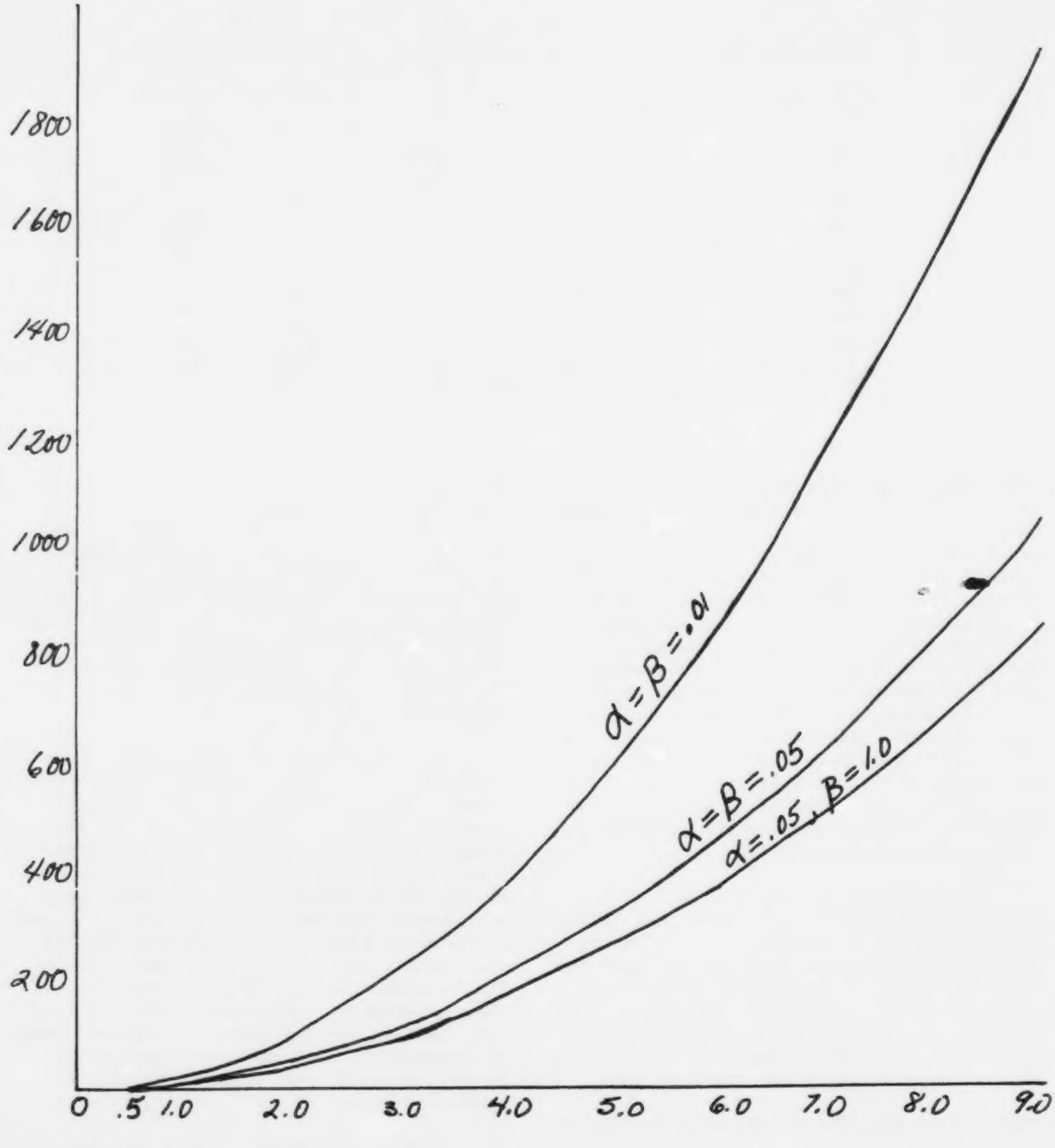


Figure 1. Sample Size as a Fraction of the σ/d Ratio for Three Combinations of α and β Levels

TABLE 2. SAMPLE SIZE AS A FUNCTION OF THE σ/d RATIO FOR THREE COMBINATIONS OF α AND β LEVELS

$\alpha = \beta = .01$		$\alpha = \beta = .05$		$\alpha = .05$ $\beta = .10$	
n	$\frac{\sigma}{d}$	n	$\frac{\sigma}{d}$	n	$\frac{\sigma}{d}$
6	0.5	3	0.5	3	0.5
11	0.67	6	0.67	5	0.67
24	1.0	13	1.0	11	1.0
54	1.5	30	1.5	24	1.5
96	2.0	52	2.0	42	2.0
151	2.5	82	2.5	66	2.5
217	3.0	117	3.0	95	3.0
603	5.0	325	5.0	265	5.0
868	6.0	468	6.0	382	6.0
1,542	8.0	832	8.0	678	8.0
2,410	10.0	1,300	10.0	1,060	10.0

The sample size has been calculated as if there were a single estimate of σ^2 although indications from the two land treatment sites measured are that σ_A^2 and σ_C^2 are unknown before the pilot test and unequal. This is known as the Aspin-Welch problem. A solution is to calculate the estimated sample size for each area, n, using a pooled estimate of σ, double the sample size estimate to 2n and adjust the individual area sample sizes based on the ratio of their standard deviations. The sample size obtained in this manner will satisfy the requirements for the specified α and β levels and any error will be on the conservative side further reducing the probability of Type I and Type II Error.

A final note on sample size. If a two-stage sampling plan is used, the first stage may be taken with $n_A - n_C$. The second stage may then be adjusted to yield the required number of soil samples and the proper ratio of control to application soil samples. A second stage may not always be necessary, but must be based on the results of the first stage of the sampling plan.

STATISTICAL ANALYSIS OF SOIL SAMPLE RESULTS

The original analysis plan called for performing a nested analysis of variance (ANOVA) for each site to calculate the effects of both treatment and depth nested within treatment. The descriptive statistics, however, showed the cell standard deviation to be highly variant. Therefore, combining the variance estimates in an ANOVA would violate the hypothesis of equal cell variances and cause heteroscedasticity. Rather than weighting the ANOVA to adjust the variances, a two sample t-test was performed comparing the average concentrations between treatment and control for each depth. The mean concentrations and conductivity for each depth at sites A and B are displayed in Table 3.

The results of the t-tests are shown in Table 4. It is interesting to note that almost all of the application/control differences were significant at the .05 level, showing an almost complete separation between application and control areas. The chemicals for which the t-tests were not significant are underlined in Table 4. Any differences between the variances for the application and control areas was automatically accounted for by the denominator of the t-statistic. This was one of the reasons that it was the ideal statistical test to compare the mean concentration in the application and control areas at land treatment sites.

To obtain a better idea of the variability of the data relative to the mean concentration of the chemicals, the coefficient of variation ([standard deviation/mean] x 100) was calculated for each chemical concentration and conductivity at both sites, at both depths, and for application

TABLE 3. AVERAGE CONCENTRATIONS (PPM) FOR APPLICATION AND CONTROL AREAS

		Site 1		Site 2	
		Depth 1	Depth 2	Depth 1	Depth 2
Copper	Application	8.98	10.54	57.67	22.93
	Control	11.26	9.61	10.11	10.57
Nickel	Application	10.17	10.37	20.34	17.98
	Control	9.49	10.99	15.09	17.61
Lead	Application	9.78	9.36	58.04	20.12
	Control	8.51	8.12	10.59	10.57
Zinc	Application	52.79	53.19	296.30	105.33
	Control	48.49	50.61	59.75	59.52
Sodium	Application	340.85	347.32	814.50	936.65
	Control	252.20	283.55	330.50	530.45
Conductivity	Application	535.42	432.50	2581.00	2098.50
	Control	212.50	216.15	243.25	239.75
Chromium	Application	18.27	21.69	757.35	198.87
	Control	17.53	20.80	47.50	54.90

TABLE 4. t-TEST VALUES FOR TESTS OF DIFFERENCES BETWEEN APPLICATION AND CONTROL AREAS

	Site 2	
Chemical	Depth 1 0-6 Inches	Depth 1 6-12 Inches
Copper	9.91	4.43
Nickel	6.79	.32
Lead	6.34	3.46
Zinc	11.67	3.34
Sodium	5.62	1.98
Conductivity	8.52	4.35
Chromium	11.18	3.78

	Site 1	
Chemical	Depth 1 0-6 Inches	Depth 2 6-12 Inches
Copper	-.91	.76
Nickel	1.31	-1.36
Lead	4.00	2.32
Zinc	2.31	1.04
Sodium	6.37	3.23
Conductivity	15.81	11.75
Chromium	.34	.36

NOTE: Positive values indicate higher application area concentrations than control areas. All differences are significant at .05 level except those underlined.

TABLE 5. COEFFICIENTS OF VARIATION EXPRESSED AS A PERCENTAGE: $\frac{\sigma}{\overline{X}} \times 100$

		Site 1		Site 2	
		Depth 1	Depth 2	Depth 1	Depth 2
Copper	Application	16	76	37	54
	Control	99	30	8	11
Nickel	Application	15	21	14	24
	Control	22	15	12	16
Lead	Application	19	39	58	61
	Control	11	13	10	12
Zinc	Application	20	31	30	55
	Control	12	12	22	33
Sodium	Application	19	18	40	87
	Control	20	28	61	79
Conductivity	Application	18	23	47	91
	Control	34	27	59	41
Chromium	Application	35	31	37	85
	Control	51	49	14	20

and control areas. The coefficients of variation are shown in Table 5.

No pattern for variability of the data emerges. The question of whether variation was proportional to the concentration was raised; however, the entries in the table are not consistent. The coefficient of variation did not vary proportionally with the chemical concentration. Furthermore, there was no trend in the data by application versus control, depth, or site. The range for the coefficients of variation was from 8 percent up to 99 percent. In conclusion, the coefficients of variation did not shed any light on the diffusion of chemicals in the soil or soil variability.

It also was assumed in the previous analyses that samples taken anywhere in a given plot at a given depth are all from the same statistical population. However, it could be postulated that the internal area of a test plot may have more of less concentration of chemicals, or a higher or lower variation in concentration. This possibility has been tested using the same two sample t-test which studies differences between application and control areas and between depths.

The results for Site A and Site B are displayed in Table 6. Each value is an approximate t statistic at a given depth for a given test area. Positive values indicate that perimeter concentrations averaged higher than interior concentrations. At the .05 level, the null hypothesis* ($\overline{X}_p = \overline{X}_i$) was accepted for nearly all tests performed, since the test statistics were nearly all less than 2 in absolute value.

The instances where the differences were apparently significant are infrequent enough to fall within the bounds of random fluctuation. In particular, a total of 56 t-tests were performed for the two sites with 6 tests showing apparently significant differences. This is only slightly above the expected rate of false significance if there really was no difference between perimeter and interior samples. However, there is evidence that lead and zinc concentrations in the interior of the Site 1 application area were higher than perimeter concentrations.

---

*H_o: perimeter concentration, $\overline{X}_p$ = interior concentration, $\overline{X}_i$

H: $\overline{X}_p \neq \overline{X}_i$

TABLE 6. t-TEST VALUES FOR TESTS OF DIFFERENCES BETWEEN PERIMETER AND INTERIOR SAMPLES

		Site 1		Site 2	
		Depth 1	Depth 2	Depth 1	Depth 2
Copper	Application	-3.61	-1.86	1.05	.62
	Control	1.05	1.53	-.38	-1.21
Nickel	Application	-1.43	-1.00	-.27	-.40
	Control	1.20	.12	-.50	-.85
Lead	Application	-2.63	-2.58	-.40	.31
	Control	.65	.85	-.59	-1.25
Zinc	Application	-3.21	-2.37	.60	.06
	Control	.52	.43	-1.37	-.38
Sodium	Application	1.13	-.80	1.52	1.65
	Control	.39	.49	-.27	-.21
Conductivity	Application	.74	.07	1.01	1.18
	Control	-.04	.62	1.17	-1.23
Chromium	Application	-.16	.20	.71	.78
	Control	1.21	2.41	-1.07	-2.27

NOTE: Positive values indicate higher perimiter concentrations than interior concentrations. Significant differences are underlined.

A visual inspection of the perimeter versus the interior standard deviations also indicate no systematic differences. Apparently, little or none of the variation in chemical concentration can be attributed to differences between perimeter and interior areas.

CONCLUSIONS AND RECOMMENDATIONS

1. Based on analysis of soil samples from the two land farm sites, it is possible to test for and measure significant differences in chemical concentrations between application and control areas of each land farm.

2. It is possible to guard against committing the serious error of finding no significant difference between application and control areas when in fact, one exists.

3. The proper statistical test to use is a two sample t-test.

4. The sample size, the number of soil samples from each area, can easily be determined.

5. The crucial decision in choosing the size (number of soil samples) is how big a difference in concentrations between the areas must be found before it is considered significant. Of the several possibilities available, such as the detection limit, a percentage of the mean, an arbitrary fixed amount, or a percentage of the standard deviation, choosing one standard deviation as the minimum significant difference is the most stable, simple to use, and efficient criterion. In all cases for the two land treatment sites tested, the one standard deviation criterion demonstrates a significant difference where one exists.

6. A modification of a systematic two-stage sample appears to be the most efficient and economical method of sampling. Starting with a sample size of 10 to 13 soil samples, the sample size can be adjusted to the necessary number of soil samples for the next round of sampling.

FACTORS INFLUENCING THE BIODEGRADATION OF API SEPARATOR SLUDGES APPLIED TO SOILS

K. W. Brown, K. C. Donnelly, J. C. Thomas and L. E. Deuel, Jr.
Texas Agricultural Experiment Station
Soil and Crop Sciences Department
Texas A&M University
College Station, Texas 77843

ABSTRACT

Biodegradation of the organic components of hazardous industrial wastes is essential for complete disposal. Information on the rates of degradation as a function of edaphic and management factors is necessary in order to properly design a land treatment system and to estimate the level of management and the length of time to achieve closure following the last application.

The influence of various environmental parameters on biodegradation of a refinery and a petrochemical waste was evaluated using a continuous flow soil respirometer. Biodegradation rates of the two wastes were measured by collecting CO_2 evolved and residual hydrocarbon analysis. The microbial population was determined six months after incubation had begun. The environmental parameters studied included soil texture, soil moisture, mineral nutrient amendments, application rates, application frequency and temperature. Maximum degradation rates were achieved with the Norwood sandy clay at a temperature of 30°C. The half life of the refinery sludge was 141 days, while that of the petrochemical waste was 692 days. The addition of mineral nutrients was not effective in increasing the rate of biodegradation of the refinery waste, but did produce a small increase in the biodegradation rate of the petrochemical waste. Degradation was generally optimum at field capacity and decreased when the soil moisture content was greater or lower than this level.

INTRODUCTION

Soil is increasingly being utilized as a medium for the disposal of municipal and industrial wastes. The objectives of such disposal include the recycling of water and nutrients, the decomposition of organic fractions and the adsorption and inactivation of environmentally undesirable constituents. While the effects of addition of water, salts, and nutrients to the soil is well understood, and there is an increasing body of information on the fate of metals applied to soils, much less information is available on the decomposition rate of added organics, or the factors which influence these rates.

By optimizing application rates and the controllable environmental parameters, biodegradation of hydrocarbons by soil microorganisms may be maximized, thus making land treatment an environmentally acceptable alternative for disposal of oily sludge. Previous studies by Francke and Clark (1974) reported degradation rates up to 100 bbl./ac./mo. when used crankcase oil was applied to fertilized soils; however, a study by Raymond et al. (1976) found rates of oil biodegradation to be no greater than 20 bbl./ac./mo. The rate and extent of the biodegradability of an oil sludge is dependent on the relative proportions of susceptible and recalcitrant hydrocarbons (Bartha and Atlas, 1973). The biodegradation rate of an oily waste in soils was doubled with the addition of nitrogen and phosphorus (Kincannon, 1972), while a separate study by Raymond et al. (1976) showed that the addition of fertilizer only increased oil losses following prolonged incubation as compared to unfertilized cases. In addition, Dibble and Bartha (1979a) found that higher sludge application rates favor the biodegradation of the more recalcitrant aromatic and asphaltic fractions.

The discrepancies between degradation rates in the various studies is considered to be a function of the varying composition of the oily sludge and the properties of the receiving soil. In an attempt to rectify these discrepancies, we have utilized both a refinery and petrochemical sludge to study the affect of several environmental parameters on degradation of oily sludges in four soils. The parameters studied were soil texture, soil moisture, incubation temperature, application rate, application frequency and nutrient additions.

EXPERIMENTAL DESIGN

API separator waste was collected from a petroleum refinery and a petrochemical plant for use in a laboratory biodegradation study. Separate experiments were conducted by mixing each waste with four different soils. The soils were selected to represent a range of physical characteristics. The soil-waste mixture was placed in a controlled temperature incubation chamber and incubated for periods of 180 and 360 days.

Biodegradation rates of the two wastes were studied at three temperatures, three soil moisture contents, and with varying amounts of mineral nutrients. In addition, application rates and frequency were varied to determine their effect on the biodegradation of the oily waste.

Throughout the study period, CO_2 evolved from the waste amended soil was adsorbed in columns of NaOH. Cumulative CO_2 evolution was determined at frequent intervals by titration of the NaOH solutions. At the end of each study, soil was removed and analyzed for total carbon or residual hydrocarbon. Selected soils were also analyzed for microbial populations.

EXPERIMENTAL PROCEDURES

Soil

Four soils were selected to represent a range of soil textures. They were Norwood sandy clay (Typic Udifluvent), Nacogdoches clay (Rhodic Paleudalf); Lakeland sandy loam (Typic Quartzipsamment) and Bastrop clay (Udic Paleustalf). Characteristics of each soil are given in Table 1. Detailed studies were conducted using the Norwood sandy clay soil using all levels of all the parameters considered. The other three soils were initiated only at the optimum level of each controlled parameter.

Sludge

Two API separator sludges, one from petroleum refinery and one from petrochemical plant were selected for this study. Total carbon of the two wastes was determined by wet combustion to be eleven and 35%, respectively. The nitrogen content of each waste was determined by the Kjeldahl method described by Bremner (1965). The refinery waste contained 0.09% N while the petrochemical waste had 0.11%. The refinery waste contained 21.4% decantable liquid, while the petrochemical waste was 12.5% decantable liquid. To facilitate handling and assure that representative amounts of these fractions of the waste were applied to each treatment, the liquid phase was decanted from each waste and each component was measured separately, and recombined prior to application.

Water content was determined by distillation, and the solvent extractables were quantified gravimetrically following Soxhlet extraction with the respective solvents. Pentane, benzene and dichloromethane were used to extract the saturates, aromatics and asphaltics respectively. Residues were heated at 750°C for ash content. Wet combustion with potassium dichromate and $H_2SO_4:H_3PO_4$ yielded total C by gravimetric analysis of CO_2 evolution. The constituents of both wastes are given in Table 2.

Selected soil samples were analyzed for residual hydrocarbon content following

TABLE 1. CHARACTERISTICS OF SOILS UTILIZED IN BIODEGRADATION EXPERIMENTS

Soil Series	Sand	Silt	Clay	OM	CEC meq/100g	pH	N	P	K	Ca	Mg	% Moisture		
	%						ppm					WP	FC	SAT
Norwood	48.2	15.2	36.6	1.4	19.6	7.69	Low	94	312	4000	485	12	18	33
Nacogdoches	41.8	12.9	45.3	1.3	17.2	7.95	Low	3	164	1280	400	8	20	36
Lakeland	81.1	4.5	14.4	0.7	0.3	6.45	Low	20	200	600	100	1	5	23
Bastrop	60.3	10.0	29.7	1.0	27.4	6.86	Low	25	200	2920	385	6	22	25

TABLE 2. CHARACTERISTICS OF THE SLUDGES

Oil Sludge	Extractable Carbon g C/100g	Ash	Water	CLASS % OF TOTAL HYDROCARBON		
				Pentane	Benzene	Dichloro-methane
Refinery	10	41	46	72	22	6
Petrochemical	62	25	12	63	36	1

incubation in the soil respirometer. A 25 g sample was mixed in a Waring blender with 25 g anhydrous Na_2SO_4. To this, 150 ml of diethyl ether was added followed by blending for one minute. The ether was decanted and filtered using a Buchner funnel and Whatman No. 42 filter paper. This extraction was repeated twice with 50 ml diethyl ether and transferred to another Buchner funnel. The extract was refiltered until all soil particles were removed, and then transferred with rinsing into a tared round-bottom flask. The solvent was evaporated in a Brinkman-Buchi Model Roto-Vapor-R* and the extractable hydrocarbons determined gravimetrically.

Biodegradation

The rates of biodegradation were determined in respirometers in which the soils were incubated at controlled temperature. A continuous stream of CO_2-free air passed over the soil in the incubation flasks, and the evolved CO_2 was collected from the air leaving each flask in columns containing 0.1N NaOH. A schematic diagram of the apparatus is shown in Figure 1. Generally, each treatment was replicated.

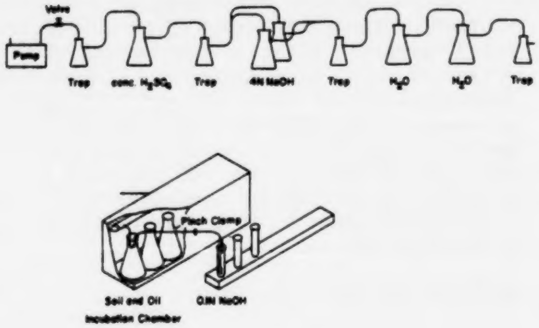


Figure 1. Schematic diagram of a respirometer.

Apparatus consisting of concentrated H_2SO_4, 4N NaOH and CO_2- free water was used to remove CO_2 and other carbon compounds and to provide a water saturated air stream for each incubation flask (Stotzky, 1960; Stotzky, 1965). Twelve flasks were placed in each controlled temperature incubation chamber, 18 x 34 in. constructed from 3/4" styrofoam. A coil of copper tubing connected to a water bath was used to provide temperature control. For experiments run at 10°C, sand was used in the bottom of the chamber to provide thermal contact with the soils.

The equivalent of 100 g of dry soil was crushed on a glass plate. A 20-25 g subsample of the soil was placed in an evaporating dish and the waste added on a percent weight basis. After thorough mixing, the total soil sample was mixed and placed in a pre-weighed 500 ml Erlenmeyer flask. The exhaust air passed through an NaOH trap. The accumulated CO_2 was determined by titration (Stotzky, 1965).

Soil Moisture

Soil samples above field capacity were dried to reach field capacity, while samples collected below field capacity were wetted with the required amount of distilled water to reach field capacity prior to waste application. Field capacity for the four soils was 18%, 5%, 22% and 20% for the Norwood, Lakeland, Bastrop and Nacogdoches, respectively. In addition, samples of the Norwood soil were tested at moisture contents of 33% and 12%. The incubation flasks were reweighed periodically, and moisture contents were adjusted as needed.

---

* Mention of brand name does not constitute endorsement.

Temperature Effects

The effect of temperature on degradation of the two sludges was studied by incubation of the soil-sludge mixtures at 10, 30 and 40°C. Each waste was studied at five loading rates at each temperature.

Application Rates

Application of oil sludge to soils was studied at treatment rates of 0.1,0.5,1.0,5, and 10 grams of sludge per 100 grams dry weight of soil, equivalent to a hydrocarbon loading of 11, 55, 110, 550 and 1100 mg refinery or 35, 175, 350, 1750 and 3500 mg petrochemical waste. Control soils to which no sludge had been applied were included in each study to monitor the respiration rate of the indigenous soil microorganisms.

Application Frequency

Two experiments were conducted to determine the effect of repeated applications of waste sludge on the degradation rates. In the first experiment, reapplications of the petrochemical waste were made following 180 days of decomposition, corresponding to the initial application rates of 0.1, 0.5, 1 and 5 g per 100 g soil. In the second experiment, reapplications were made at a rate of 5 g per 100 g soil 45, 90 and 135 days after the initial application to two flasks of each waste and 90 days after the initial application to one flask of each waste. One flask of each waste served as a control receiving 5 g per 100 g soil at the beginning of the experiment.

Mineral Nutrients

The C:N ratio of the refinery and petrochemical wastes was determined to be 110:1 and 350:1 respectively. In an attempt to improve the microbial activity, mineral nutrients were added in the form of $Ca(NO_3)_2$, KCl and $Ca_3(PO_4)_2$. These were mixed with the soil prior to addition of the wastes to achieve the desired treatment ratios. The refinery wastes were tested at C:N ratios of 100:1, 50:1 and 10:1, and C:K and C:P ratios were 50:1. In addition, one flask was supplied with N, P, and K at ratios of 50:1. The C:N ratios of the petrochemical wastes studied were at 300:1, 150:1 and 20:1. The C:P and C:K ratios of the soils in two flasks were adjusted to 150:1 and the soils in another flask were adjusted to 150:1 for all their nutrients.

RESULTS AND DISCUSSION

Initial results indicated that a flow rate of at least 20 ml of air per minute per 100 grams of soil was required to prevent depletion of oxygen in the incubation flasks. Reproducibility was increased when each flask was removed at 45 day intervals and the soil moisture content determined by weighing. When the moisture content of the soil fell below 10% or increased to above 35%, the respiration rate deviated from replications in which the moisture content had not changed, and such data were rejected.

Soils Comparison

Four soils were studied to determine their utility as a site for the landfarming of oily sludges. Each was incubated at 30°C at field capacity moisture content. The results are presented in Figures 2 and 3 and in Table 3. For both wastes, the greatest amount of degradation occurred in Norwood soil, while degradation in the Nacogdoches and Lakeland soils was intermediate, with the least amount occurring in the Bastrop soil. The amount of carbon evolved as CO_2 from petrochemical sludge-amended Bastrop clay was only 7 mg greater than from the unamended soil, this is equivalent to a decrease of only 0.4% total carbon. Twenty-five percent of the refinery, and 5% of the petrochemical waste decomposed from the Lakeland soil

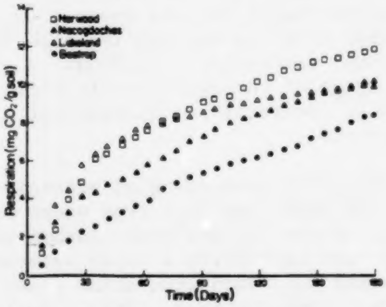


Figure 2. The effect of soil texture on CO_2 evolution from soils amended with 5% (wt./wt.) refinery waste and incubated for 180 days at field capacity and 30°C.

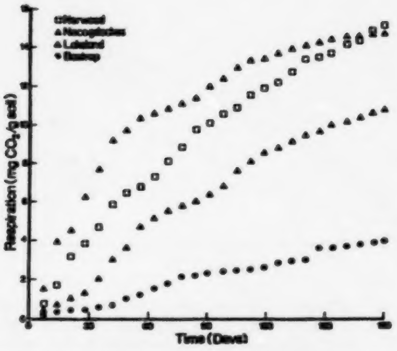


Figure 3. The effect of soil texture on CO_2 evolution from soils amended with 5% (wt./wt.) petrochemical waste and incubated for 180 days at field capacity at 30°C.

during the 180-day incubation period; while 29% and 10% of the refinery and petrochemical sludges, respectively, were decomposed in the Nacogdoches soil. The order of decomposition was not influenced by the pH of the soils. This may have been due to the random range of pH of the soils.

Soil Moisture

The influence of soil moisture on the average biodegradation rates at 30 and 40°C is given in Figures 4 and 5. For both wastes, the moisture content had a

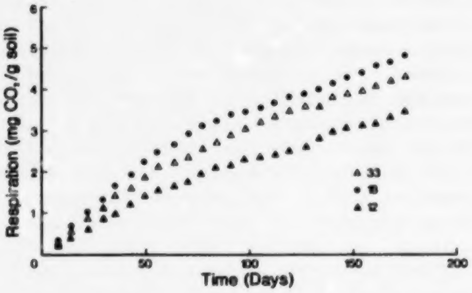


Figure 4. The influence of soil moisture on CO_2 evolution from Norwood soil amended with 1% (wt./wt.) refinery waste and incubated for 180 days at 35°C.

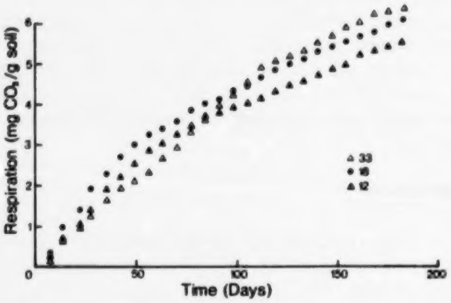


Figure 5. The influence of soil moisture on CO_2 evolution from Norwood soil amended with 1% (wt./wt.) petrochemical waste and incubated for 180 days at 35°C.

TABLE 3. EFFECT OF SOILS ON THE BIODEGRADATION OF BOTH WASTES APPLIED AT 5% AT FIELD CAPACITY, INCUBATED FOR 180 DAYS AT 30°C

Soil	Determined by CO_2 Evolution		
	Carbon Applied (mg)	Carbon Degraded (mg)	Carbon Degraded Percent of Waste Applied
Refinery			
Norwood	550	218	40
Nacogdoches	550	158	29
Lakeland	550	136	25
Bastrop	550	134	24
Petrochemical			
Norwood	1750	293	17
Nacogdoches	1750	173	10
Lakeland	1750	92	5
Bastrop	1750	7	0.4

greater relative influence on the rate of biodegradation at 10°C than it did at the higher temperatures. At both temperature regimes, the refinery waste exhibited maximum degradation at 18% moisture which represented field capacity. The biodegradation rates were less at both wetter and drier moisture contents. For the petrochemical waste, the maximum biodegradation rates occurred at the lowest moisture content at the low temperature and at the highest moisture content for the high temperature. Thus, while field capacity appeared to be the optimum soil moisture for the refinery waste, no such optimum was found for the petrochemical waste. For both wastes, there appeared to be a rather broad range of soil moisture contents including conditions both wetter and drier than field capacity which had minimal influence on the waste decomposition. Only at excessively wet or dry conditions did the moisture content become a dominant factor.

Temperature

The results of experiments to determine the effect of temperature on the biodegradation of wastes applied at a rate of 5% are shown in Figures 6 and 7. The evolution of carbon dioxide from soils treated with both wastes increased with temperature through 40°C. Increases in the respiration rate of the unamended soils between 30 and 40°C were greater than the increase in the rate of the soil to which waste had been added. Therefore, a comparison of the percentages of waste degraded at the various temperatures reveals a reduction in percentage of carbon degraded from the waste which was incubated at 40°C. Biodegradation was calculated both from CO_2 evolution and residual carbon measured by wet combustion. The wet combustion data will be used here as a basis for discussion. At 30°C, 45% of the refinery waste, and 31% of the petrochemical waste were degraded, while at 40°C only 36 and 23% of the refinery and petrochemical wastes respectively were degraded. At 10°C, respired CO_2 was equivalent to only 18 and 14% above the unamended soils for the refinery and petrochemical waste respectively.

The biodegradation rate generally doubled between 10 and 30°C but decreased again at 40°C indicating some inhibition. These results are in general agreement with those reported by Dibble and Bartha (1979a), who reported the optimum temperature for degradation of an oily sludge to be about 20°C.

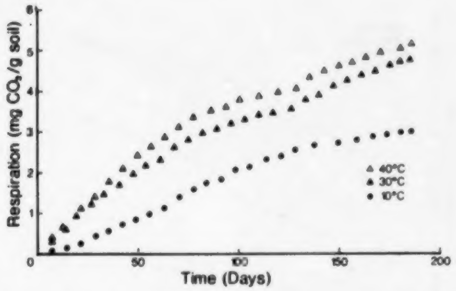


Figure 6. Effect of temperature on CO_2 evolution from Norwood soil amended with 5% (wt./wt.) refinery waste and incubated for 180 days.

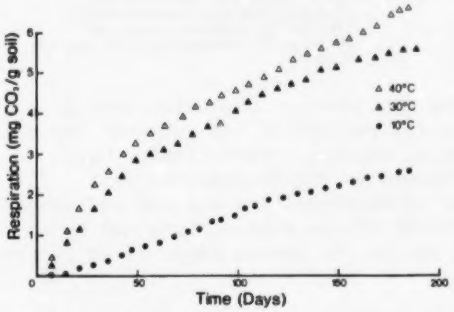


Figure 7. Effect of temperature on CO_2 evolution from Norwood soil amended with 5% (wt./wt.) petrochemical waste and incubated for 180 days.

Application Rates

The evolution of CO_2 from soils amended with either waste increased with increasing application rates shown in Figures 8 and 9 and Table 4. Since data were available from both 30 and 40°C and differed only a little, the data averaged over these two treatments are shown here.

Biodegradation of both wastes increased with increasing application. Of the two wastes investigated, a much larger fraction of the carbon applied in the refinery waste was released as CO_2. An average of 33.4 mg of the carbon applied in the refinery waste was respired, while only 13.4 mg of the petrochemical waste carbon was released.

When comparisons are made strictly on the basis of the amount of waste applied,

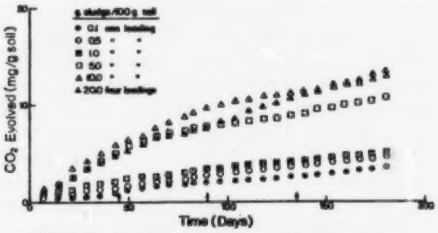


Figure 8. The influence of loading rate on the biodegradation of refinery waste applied to Norwood soil and incubated for 180 days at 30°C and 18% moisture.

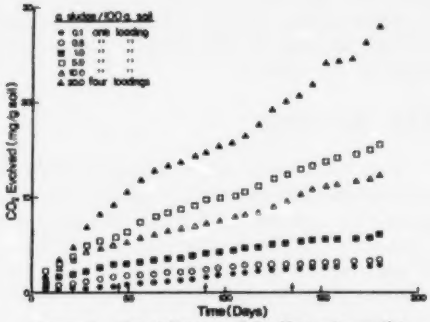


Figure 9. The influence of loading rate on the biodegradation of petrochemical waste applied to Norwood soil and incubated for 180 days at 30°C and 18% moisture.

TABLE 4. THE INFLUENCE OF LOADING RATE ON THE BIODEGRADATION OF WASTE APPLIED TO NORWOOD SOIL INCUBATED AT 35°C AND 18% MOISTURE FOR 180 DAYS

	Sludge Applied (%)	C Applied (mg)	CO$_2$ Evolution (mg)
Refinery Sludge			
1 Loading	0.1	10	10
"	0.5	55	56
"	1.0	110	34
"	5.0	550	40
"	10.0	1,100	27
Petrochemical Sludge			
1 Loading	0.1	40	12
"	0.5	180	10
"	1.0	350	19
"	5.0	1,750	17
"	10.0	3,500	9

as shown in Figure 10, it is evident that a slightly greater percentage of the petrochemical waste was degraded, particularly at the greater application rates. The respiration is nearly linear at low rates, but appears to be approaching a plateau at the greater rates. This indicates that inhibiting mechanisms decreased the fraction of the applied carbon which was respired.

The greatest fraction of the refinery waste respired when 0.5% was applied to the soil, while the greatest fraction of the petrochemical waste was released as CO$_2$ at the 1% application rate. The fractions respired do not decrease

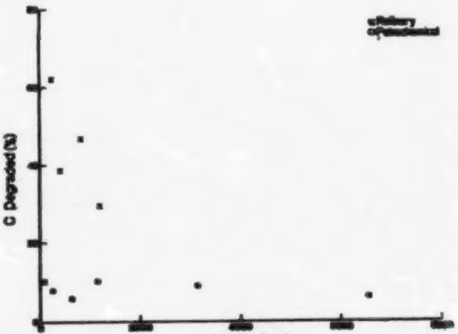


Figure 10. The effect of application rate on the degradation of refinery and petrochemical waste.

greatly at 5% of each waste, but fall at 10% ; therefore, applications of between 1 and 5% appear to encompass the maximum degradation rates.

Mineral Nutrients

The influence of nutrient addition on the respiration rates is shown in Figures 11 and 12. The two wastes differed greatly in their C:N ratios. The refinery waste was composed of 110 parts C for each part N, while the petrochemical waste had a C:N ratio of 350:1. For the refinery waste, optimum degradation occurred when the C:N ratio was reduced to 10:1. Addition of potassium to a ratio of 50:1, C:K, and supplementation with NPK at a ratio of 50:1 did not result in an increase in evolved carbon dioxide from the waste amended soil.

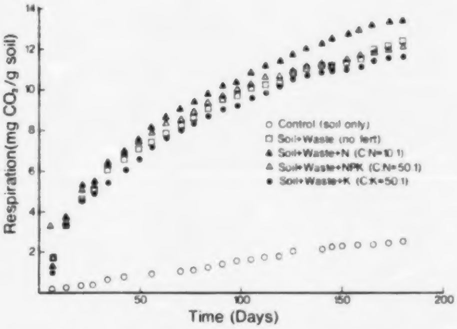


Figure 11. The influence of nutrient additions on the cumulative respiration of Norwood soil amended with 5% (wt./wt.) refinery waste and incubated for 180 days at 30°C and 18% moisture.

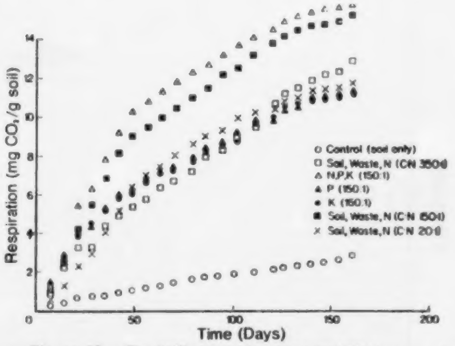


Figure 12. The influence of nutrient additions on the cumulative respiration of Norwood soil amended with 5% (wt./wt.) petrochemical waste and incubated for 180 days at 30°C and 18% moisture.

The petrochemical waste exhibited a 20% increase in CO_2 evolved as a result of N alone at a C:N ratio of 150:1 or NP and K at a ratio of 150:1 each. The addition of greater amounts of nitrogen alone did not result in an increase in respiration rates over the unamended waste treatment. As with the refinery waste, the addition of phosphorus and potassium alone did not result in an increase of CO_2 evolution. Determinations of residual hydrocarbon for the amended soil 180 days following fertilizer application also indicated increased degradation rates of some treatments as indicated by the cumulative CO_2 evolution (Table 5). The addition of nitrogen at a ratio of 10:1, C:N, increased the rate of biodegradation for the refinery waste by 6%. The addition of all three mineral nutrients at a rate of 150:1 C:NPK increased the rate of biodegradation for the petrochemical waste by 5%.

Thus, the decomposition rate of the refinery waste was increased slightly by adjusting the C:N ratio from 110:1 to 10:1. The nitrogen deficient petrochemical waste exhibited an increase in decomposition when the C:N ratio was adjusted from 350:1 to 150:1, but did not differ from the unfertilized rate when additional nitrogen was added to lower the C:N ratio to 20:1. The addition of P and K alone or with nitrogen did not increase the respiration rates from soils amended with either waste. The lack of increased biodegradation of the petrochemical waste at C:N ratios narrower than 150:1 indicates that factors other than nitrogen were limiting breakdown of the waste.

Other researchers have also reported that the addition of mineral nutrients to waste amended soil offset nutritional imbalances, thus providing a more suitable environment for the microbial utilization of petroleum compounds. Increases in the rate of waste biodegradation have been reported by Cook and Westlake (1974), Dotson et al. (1971), Maunder and Ward (1975), and Dibble and Bartha (1979b). When several different oily wastes were applied to soils, Kincannon (1972) found that the rate of biodegradation was doubled when nitrogen and phosphorus were added to the soil with the waste. In a field study on waste degradation in soil, Raymond et al. (1976) did not find an increase in the rate of biodegradation in fertilized plots until

TABLE 5. THE EFFECT OF MINERAL NUTRIENTS ON RESIDUAL CARBON IN WASTE AMENDED SOIL AFTER 180 DAYS INCUBATION

Mineral Nutrients	Residual Carbon Ether Extract (gm)	Carbon Degraded (%)
Refinery Sludge: Total carbon applied 0.55 gm		
None	0.13	76
C:P 50:1	0.12	78
C:NPK 50:1	0.14	75
C:N 10:1	0.10	82
Petrochemical Sludge: Total carbon applied 1.75 gm		
None	0.88	50
C:P 50:1	0.88	50
C:NPK150:1	0.78	55
C:N 20:1	0.88	50

a year after waste application. Dibble and Bartha (1979a) reported that excessive rates of mineral nutrient addition did not favor waste biodegradation. Atlas (1977) suggests that the best fertilizer for soil application is a form of readily usable nitrogen and phosphorus along with a form of slow release fertilizer to prevent leaching losses.

Thus the present data and that reported in the literature indicates that additions of the proper amounts of selected nutrients can increase biodegradation, while excessive amounts provide no benefit. Most of the results have indicated that nitrogen is the most needed nutrient and that additions are dependent on the waste characteristics. Dibble and Bartha (1976b) found an optimum C:N ratio of 60:1 for their oily waste, while one of those considered here exhibited an optimum of 10:1 and the other at 150:1. It would appear that optimum nutrient additions will need to be determined for each waste. Care must also be taken, however, to avoid additions of excess nitrogen fertilizer which could contribute to leaching of nitrates.

CONCLUSIONS

The rates of biodegradation of both wastes depended greatly on the soil to which they had been applied. Maximum biodegradation was found in the Norwood sandy clay soil, while the minimum was found in the Bastrop clay soil, when both were maintained at field capacity moisture content. The soils had a minimum range of pH values, and respiration rates were not correlated with this parameter. Nutritional differences could have been a factor, but fertilizer additions were not evaluated on all soils.

The soil moisture content influenced the biodegradation rates of both wastes. Field capacity was the optimum moisture content for the petrochemical waste, dependent to some extent on the incubation temperature. For both wastes, there appeared to be a broad range of moisture contents including conditions both wetter and drier than field capacity which had a minimum influence on the rate of biodegradation. The rates decreased when the soil become either too wet or too dry.

The biodegradation of both wastes increased with application rates. Inhibitory mechanisms however resulted in smaller increases in biodegradation per amount of waste applied between the 5 and 10% application rates. Biodegradation of the applied wastes increased through 30°C and decreased slightly at 40°C. The biodegradation rate at 10°C was about half of the maximum found at 30°C.

The rates of CO_2 evolution were similar for both wastes at the same application rates, but since the petrochemical waste contained almost four times more carbon than the refinery waste, the fraction of applied carbon respired was much less for the petrochemical waste.

Respiration rates for both wastes applied to the soil increased with application rate, but the increases were less than proportional to the amounts applied at the 5 and 10% application rates.

Small frequent applications of both wastes increased respiration rates per unit applied over that obtained on a single equivalent application. While repeated applications resulted in a greater total respiration, the fraction of the applied carbon which was released as CO_2 decreased at increasing application rates. Thus, biodegradation rates of subsequent applications per amount applied were less than those of the first applications.

Adjustments in the C:N ratio by the addition of fertilizer nitrogen increased the rate of biodegradation. The petrochemical waste, which contained a large fraction of carbon, exhibited the greatest degradation rate at a C:N ratio of 150:1; while the refinery waste, which contained less carbon and more nitrogen, exhibited a small increase in biodegradation rate when the C:N ratio was adjusted from 111:1, the original, to 10:1. Additions of P and K either alone or with nitrogen did not increase the rates of biodegradation of either waste.

Microbial analysis revealed that both hydrocarbon utilizing bacteria and fungi are present in the unamended soils. Additions of either waste resulted in increased populations of hydrocarbon utilizing bacteria and fungi. The greatest populations of both were found in soil to which 1% by weight of the sludge had been added. Populations were diminished at greater application rates, and at the 10% level, the population generally decreased below levels found in unamended soils.

REFERENCES

1. Atlas, R. M. 1977. Simulated Petroleum Biodegradation. Crit. Rev. Microbiol. 5: 271-386.
2. Bartha, R. and R. M. Atlas. 1973. Degradation of oil in seawater: Limitting factors and artificial stimulation in the microbial degradation of oil pollutants. D. G. Ahearn and S.P. Meyers (ed.). Center for Wetland Resources, Louisiana State Univ., Baton Rouge, LA. Publ. #LSU-S. G-73.01.
3. Bremner, J. M. 1965. Total Nitrogen. In Methods of Soil Analysis, Chemical and Microbiological Properties, Part 2. C. A. Black (ed.) pp. 1149-1176. American Society of Agronomy.
4. Cook, F. D., and D. W. S. Westlake. 1974. Microbial Degradation of Northern Crude Oils. Information Canada Cat. No. R72-12774.
5. Dibble, J. T. and R. Bartha. 1979a. Effect of environmental parameters on biodegradation of oil sludge. Appl. Environ. Microbiol. 37: 729-738.
6. Dibble, J. T. and R. Bartha. 1979b. Leaching aspects of oil sludge biodegradation in soil. Soil Sci. 127: 365-370.
7. Dotson, G. K., R. B. Dean, W. B. Cooke and B. A. Kenner. 1971. Land spreading, a conserving and non-polluting method of disposing of oily wastes. In Proc. 5th Int. Water Pollution Research Conf. Pergamore Press, New York.
8. Francke, H.C. and F. E. Clark. 1974. Disposal of oily waste by microbial assimilation. U.S. Atomic Energy Report Y-1934.
9. Kincannon, C. B. 1972. Oily Waste Disposal by Soil Cultivation Process. Report EPA-R2-72-100. U.S. Environmental Protection Agency, Washington D.C.
10. Maunder, B. R. and J. S. Ward. 1975. Disposal of Waste Oil by Landspreading. In 3rd Int. Biodegradation Symposium. August 17-23, 1975. Univ. of Rhode Island, Kingston, TS XXV-5.
11. Raymond, R. L., J. O. Hudson, and V. W. Jamison. 1976. Oil Degradation in Soil. Appl. Environ. Microbiol. 30: 522.
12. Stotzky, G. 1960. A Simple Method for the Determination of the Respiratory Quotient of Soils. Can. J. Microbiol. 6: 439-452.

13. Stotzky, G. 1965. Microbial Respiration. In Methods of Soil Analysis, Chemical and Microbiological Properties. C. A. Black (ed.). Part 2, pp. 1550-1572. American Society of Agronomy.

REVIEW AND PRELIMINARY STUDIES OF INDUSTRIAL LAND TREATMENT PRACTICES

Rufus L. Chaney
Sharon B. Hornick
Lawrence J. Sikora
USDA-SEA-AR
Biological Waste Management & Organic Resources Laboratory
Beltsville, Maryland 20705

ABSTRACT

This paper discusses the planned efforts of the Biological Waste Management and Organic Resources Laboratory to conduct research on the land treatment of various hazardous wastes through an Interagency Agreement with the U.S.E.P.A. The effort began with a critical review of information relevant to land treatment, with the first draft now completed. The overall plans of the Agreement includes research on the fate and effect of organic and inorganic waste constituents in the environment with studies in the greenhouse, in the laboratory, on new field plots, and on field plots at existing land treatment sites.

A review of natural controls which limit the adverse effects of heavy metals in wastes is also presented. For most elements, the "Soil-Plant Barrier" protects the food chain. However, humans or livestock can suffer health effects from mismanaged wastes containing elevated levels of Cd, Se, Mo, Pb, and Co. Lastly, as an example, a discussion of Cr in hazardous wastes, soils, plants, and animals is presented along with the specific consideration of land treatment of leather manufacturing wastes.

Introduction

In March 1980, our laboratory began a 5-year scientific study concerning the land treatment of hazardous wastes under an Interagency Agreement (IAG) with the U.S.E.P.A. Since 1971, our laboratory has studied various aspects involving the land application of sewage sludge. Some of these areas are: trenching; composting; the utilization of municipal wastes on cropland, gardens, and pastures; and the fate of nutrients, pathogens, toxic organics, and heavy metals in the environment. The aerated pile method of controlled composting was also developed in our group. Our interdisciplinary research program involved engineers, microbiologists, and soil and plant scientists.

Because of this research experience, EPA decided that our interdisciplinary approach in the study of land treatment of wastes could assist them in the development of land treatment technology and regulations. Although pesticide, petroleum, and other "hazardous" wastes have been land-applied for over 25 years, little scientific data is available to assess the efficacy and environmental acceptability of land treatment.

Scope of Research Program

In order to perform cooperative research with our laboratory, an IAG which included 6 Tasks was developed. The Tasks which involved many hazardous constituents were as follows:

Task 1: Compile, review, and critically evaluate available data on land treatment of wastes for application to hazardous wastes. A 450 page draft report (20) was submitted to EPA in January 1981. The report reviewed processes in waste treatment, soils, plants, and animals which can be affected by certain constituents or waste types which are land spread. Management and research problems were also addressed for each waste.

Task 2: Evaluate treatment of selected hazardous wastes in soils, and effects on soils and plants in the greenhouse and laboratory. This task will allow our team to study the fate and effect of both organic and inorganic hazardous constituents, the transformations of bulk organic matter and plant nutrients, the relative tolerance of crops to heavy metals and toxic organics, and bioassay for site management. Hazardous wastes to be studied will depend on EPA's agreement with our conclusions in our Task 1 report, and on the recommendations from a report from A. D. Little which evaluated the land-treatability of identified hazardous wastes.

Task 3: Evaluate land treatment of selected hazardous wastes in field studies to verify the greenhouse and laboratory investigations. Research of this task will allow the field verification of results from Task 2. Here wastes which have a high probability of being land-treatable and/or have a high need for an alternative disposal method can be studied.

Task 4: Evaluate crop species and cultivars to exclude or accumulate pollutants from hazardous waste-amended soils. Some crops tolerate soil conditions where organic matter is rapidly oxidized, or soils rich in toxic organics or heavy metals. Other crops can hyperaccumulate metals, and possibly have the ash of the crop biomass sold as an ore. Still other crops may be shown to tolerate the land treatment of wastes and thus be utilized as a cover crop during the operational period.

Task 5: Evaluate crops on existing active and closed land treatment sites. Some treatment processes are time dependent; others depend on level of organic matter in the soil. Thus, examining sites used a long time ago, or over a long term, provides information unavailable through new experimental plots.

Task 6: Determine the feasibility of combining waste streams, and processing wastes (e.g., by composting) to improve land treatment of hazardous wastes. Wastes with a high C:N ratio are difficult to manage on land. Some wastes contain hazardous constituents which are volatile, or are very weakly adsorbed and thus leachable. Pretreatment by composting may prevent many management problems, and the residue may be applied on hazardous waste land treatment sites (32), or on RCRA 4004 solid waste treatment sites (30) if the hazardous constituent is sufficiently degraded.

Task 1 Report

The Task 1 report (20) covers many items in detail, and should help land treatment site managers and planners, researchers, and regulatory officials to understand the scientific principles upon which land treatment is based. It is impossible to present a brief summary of the whole report in this paper.

On the other hand, if one selected waste were discussed, the reader would have an idea of the approach of our report and know what information to expect when the final report becomes available. We have, therefore, selected Cr and leather manufacturing wastes for discussion in this paper as an example of our approach. The literature has provided considerable information, and allowed us to identify the remaining research needed to support the land treatment of Cr-rich wastes.

Routes for Environmental Impacts

Research has shown that the food-chain can be influenced by a waste-applied hazardous constituent through: 1) direct ingestion of the waste, 2) ingestion of spray-applied waste adhering to crops, 3) ingestion of the waste lying on the soil surface or waste-amended surface soil, 4) ingestion of crops which accumulated the hazardous constituent from soil, 5) ingestion of animal tissues enriched in the hazardous constituent after the animal consumed the crops or wastes, or 6) ingestion of groundwater enriched in the hazardous constituent through leaching from the waste amended soil.

A committee from the National Research Council (61) recently the literature on mineral tolerance of domestic animals (Table 1). If land application of wastes could cause an element to be higher in forage crops than tolerated by livestock, or higher in vegetable crops than tolerated by humans, a potential would exist for adverse environmental impacts. Table 1 also shows the level of an element present in a crop when the crop is substantially or visibly injured (25% yield reduction) by the element (phytotoxicity). If soil and plant processes keep the level of the element in forages below that injurious to animals, then a "Soil-Plant Barrier" has protected the food chain (19,20).

For nearly all elements, the food chain is protected under worst case conditions. For a few more elements, one must rely on dietary interactions which increase tolerance in order to assert that the food chain is protected. But for Cd (in humans), Pb (in children and livestock which consume soil), and Cd,

TABLE 1. MAXIMUM TOLERABLE LEVELS OF DIETARY MINERALS FOR DOMESTIC LIVESTOCK IN COMPARISON WITH LEVELS IN FORAGES

Element	"Soil-Plant Barrier"	Level in Plant Foliage[1]		Maximum Levels chronically tolerated[2]			
		Normal	Phytotoxic	Cattle	Sheep	Swine	Chicken
		---mg/kg dry foliage---		----------mg/kg dry diet---------			
As	yes	0.01-1	3-10	50.	50.	50.	50.
B	yes	7-75	75	150.	(150.)	(150.)	(150.)
Cd[3]	Fail	0.1-1	5-700	0.5	0.5	0.5	0.5
Cr^{3+}	yes	0.1-1	20	(3000.)	(3000.)	(3000.)	3000.
Co	Fail?	0.01-0.3	25-100	10.	10.	10.	10.
Cu	yes	3-20	25-40	100.	25.	250.	300.
F	yes?	1-5	-	40.	60.	150.	200.
Fe	yes	30-300	-	1000.	500.	3000.	1000.
Mn	?	15-150	400-2000	1000.	1000.	400.	2000.
Mo	Fail	0.1-3.0	100	10.	10.	20.	100.
Ni	yes	0.1-5	50-100	50.	(50.)	(100.)	(300.)
Pb[3]	yes	2-5	-	30.	30.	30.	30.
Se	Fail	0.1-2	100	(2.)	(2.)	2.	2.
V	yes?	0.1-1	10	50.	50.	(10.)	10.
Zn	yes	15-150	500-1500	500.	300.	1000.	1000.

1/ Based on literature summarized in Chaney et al. (20).

2/ Based on (61). Continuous long-term feeding of minerals at the maximum tolerable levels may cause adverse effects. Levels in parentheses were derived by interspecific extrapolation by NRC.

3/ Maximum levels tolerated based on human food residue consideration.

Mo, Se, and Co (in livestock and wildlife), the "Soil-Plant Barrier" does not adequately protect the food chain. However, as is discussed below, the food chain is adequately protected from Cr in wastes applied to land.

Chromium in Hazardous Wastes

Many wastes contain Cr. EPA identified electroplating sludges (F006), Cr pigment wastes (K002-008), petroleum sludges (K048-051), tannery wastes (K053-058), and a few other wastes (K061, 062, 063, 069, and 074) as hazardous because they contained Cr (31). Only tannery wastes (K053-058) and processed titanium ore wastes (K074) were subsequently delisted (34) when the EP test was changed to reflect chromate rather than total Cr (33). The Cr in petroleum sludges and many others began as chromate used in cooling towers as a corrosion inhibitor, but was subsequently reduced to an insoluble chromic form in the anaerobic organic wastes. As will be discussed below, chromate smelting wastes can be high in chromate, as well as a few wastes not listed by EPA.

Chromate in wastes is a risk to humans since chromate has been found to be carcinogenic to industrially exposed workers. Thus, the fate of Cr in wastes, soils, plants, and animals has to be considered in planning land treatment sites for Cr-rich wastes. Transforming any chromate in a waste to chromic is a necessary part of the waste handling program if land treatment is planned.

Chromium in Soils, Plants, and Animals

Chromium is not essential for plants (42), but chromium is essential for animals (59, 61, 81). An organic chelated Cr^{+3} compound (78) is a cofactor in insulin hormone response controlling carbohydrate metabolism. Human diets are often deficient in this Cr compound, and some older humans presently experience Cr deficiency (61, 81).

Chromium exists in two redox forms in nature: chromic (Cr^{3+}) and chromate (Cr^{6+}). Bartlett and Kimble (12) show an Eh-pH diagram for Cr in water. Chromium in soil solution is further decreased since chromic is strongly adsorbed and chelated by soils at all practical pH levels (12, 18, 38). Chromate is rapidly reduced to chromic in soils; reduction is more rapid in acidic soils (13, 18, 38).

Bartlett and James (11) discovered that *soluble* chromic could be oxidized to chromate in soils and that air drying soils prevented this reaction. Although oxidation may be important in plant uptake of Cr, it is not yet clear that chromic oxidation is significant in the natural environment since chromic is so insoluble and strongly sorbed. Recent research has shown that freshly precipitated (less crystalline) MnO_2 oxidizes the chromic, producing chromate (3, 10, 11, 75).

Plant uptake of Cr to plant shoots is generally very limited. Even when soluble chromate is supplied, it is reduced to chromic in plant roots and kept there as chelates, precipitates, or adsorbed Cr. Chromate can be quite phytotoxic (16, 21, 36, 60, 75, 80). However, even under conditions of chromate phytotoxicity, plants contain less than 10 ppm Cr (normal plant shoots are lower than 2 ppm Cr).

Because humans are often deficient in Cr, research has been conducted on methods to increase Cr in plants. Although chromate existence is more favorable at alkaline pH, adjusting soil pH had little effect. Repeated sub-phytotoxic additions of chromate to soils, or adding 1% Cr to soil as freshly precipitated $Cr(OH)_3$, did increase Cr somewhat in plant leaves, but not in grain or fruits (17, 18). Heating soils to 300°C to simulate effects of forest fires caused soil chromate to increase; corn grown in heated soil had greater Cr in roots than plants grown on unheated soils, but not in shoots (40). Most plants growing on naturally high Cr serpentine soils have only normal levels of Cr (4, 18, 65). However, some plants occurring naturally on these soils are tolerant of the low Ca status and high Ni and Cr. Both endemic and ecotypic serpentine tolerant plant species include some Cr accumulators (50, 51, 53, 70, 85).

Lyon, Peterson, and Brooks (52) found that *Leptospermum scoparium* (a Cr accumulator) translocated Cr in xylem as chromate. However, Cr in roots and shoots was chromic (49); the major identifiable soluble Cr anionic chelate was trisoxalatochromium(III) in all tissues except xylem exudate. Peterson et al. (69, 74) examined Cr uptake and translocation by barley. In contrast to the results with *L. scoparium*, chromate remained chromate in the roots; further, some chromic was oxidized to chromate by the roots, and the trisoxalatochromium(III) was not found in roots or shoots. Chromate may limit plant growth on high Cr serpentine soils. Based on the study of Anderson, Meyer, and Mayer (4), chromate in the displaced soil solution was thought to be too low to be toxic to any plants. However, this work used air-dried soils, and air-drying temporarily inhibits a soil's ability to oxidize chromic to chromate (11). Thus, the whole subject must be re-evaluated with high Cr soils not air-dried before study.

The food chain is well protected from excess Cr by the "Soil-Plant Barrier." Animals tolerate high levels of insoluble Cr components in their diet (61). Chromic oxide has actually been fed as a dietary marker for animals (61, 66, 81) and even humans (43, 84). Recently, McLellan et al. (58) showed that $^{51}Cr^{3+}$ mixed in a diet is an effective label to indicate when all (99.9% of ingested ^{51}Cr by 16 days) of a meal has finally transited the digestive system and been excreted. NRC (61) indicated that 3000 ppm Cr as insoluble Cr_2O_3 or 1000 ppm Cr as other chromic salts were tolerated by domestic animals. Because crop plants have such low Cr levels even when grown on soils very high in Cr, the food chain is protected against excess plant absorbed Cr. Animal ingestion of organic wastes rich in Cr appears to offer a similarly low hazard based on sewage sludge (45) and tannery sludge (23, 46, 83) feeding studies. Hydrolyzed leather meal (not over 2.75% Cr) is an approved feed ingredient (6).

Chromate has been found to be mutagenic (63) and carcinogenic, particularly if inhaled; humans and experimental animals exposed to chromate dusts and mists are quite susceptible to nasal cancer (61, 79). Chromate in feed has not caused similar cancer in experimental animals, and chromic in feed was not carcinogenic or mutagenic. Chromate in land-applied organic wastes is rapidly converted to chromic, greatly reducing the chance for a carcinogenic risk. In contrast, when chromate-rich inorganic wastes are placed on the land, chromate may remain for a long period (16, 36).

Land application of refuse compost, sewage sludge, tannery sludge, cooling tower blowdown, and sewage effluent can cause Cr in the surface soil to be greatly enriched. However, these practices have not yet been shown to affect Cr in soil below the tilled zone, and do not increase plant Cr after the first crop year (22, 24, 25, 26, 28, 38, 44, 60, 73, 76). Gemmell (37) and Breeze (16) found that sewage sludge and refuse compost were very effective in reducing chromate toxicity in smelter wastes.

In summary, Cr in wastes is very unlikely to cause food chain problems because animals tolerate high levels of insoluble Cr compounds in diets, and plants do not absorb and translocate high levels of Cr to edible plant tissues even when soils are greatly enriched in Cr.

Leather Manufacturing Wastes

Leather is stabilized collagen prepared from the hide of livestock. Hides are transformed into leather by two major methods: 1) chrome tanning, and 2) vegetable (polyphenol) tanning. Wastes from this industry were listed as hazardous wastes in May, 1980 (31) because of Cr, Pb, and sulfide present in the wastes. Upon reevaluation, these wastes were removed from the listed hazardous wastes (34) based on the presence of chromic rather than chromate in the wastes. The EP test was changed to consider chromate rather than total Cr (33).

This section discusses sources and nature of wastes from the chrome tanning industry, results from feeding these wastes to livestock or applying them to land, and research needs for land treatment of tannery wastes. Much of the discussion of Cr is relevant to other waste streams declared hazardous because of Cr.

Sources of Wastes

EPA and its contractors have described tannery operations, waste streams and waste disposal practices (14, 29, 68). Flesh and hair are removed in mechanical and chemical operations which use lime and sodium sulfide. Manganous salts are added to catalyze oxidation of the sulfide in dehairing wastewater (8). This Mn could also contribute to oxidation of sludge chromic to chromate (see below). It seems unwise to mix Mn-treated wastewater or sludges from dehairing processes with Cr-rich sludges from waste tanning solution or tanned hide rinse water. Segregation of these waste streams would reduce the potential for chromate production from tannery sludges. The organic matter plus lime sludge from treatment of dehairing wastewater is similar to limed raw sewage sludge, but lower in heavy metals other than Cr and Mn. This lime-organic waste sludge could be applied to cropland as a low grade limestone with low grade fertilizer value. If farmland is near the tannery, utilization of the liquid sludge on farmland should be less expensive than depositing it in a landfill. Fleshing wastes are often sold as a by-product for rendering or feed; these could be used as organic fertilizer on cropland if applied using technology to avoid malodors.

After removal of flesh from the hides, they are acidified and treated with the chrome tanning solution. The solution contains chromic sulfate at low pH. The Cr^{3+} reacts with the collagen and stabilizes it against deterioration. The waste chrome tanning solution is recycled directly in some tanneries; in others, the Cr_{3+} is precipitated by pH adjustment, collected, and reused (41, 54, 64). In others, it is discharged to the wastewater treatment system or publicly owned treatment works (POTW).

The tanned hide is rinsed, and then cut or split into grain (outer) side (used to make finished leather products), and split side (inner, or flesh side) which is used to make rougher leather products.

The grain side is "shaved" to a uniform thickness, generating a coarse particulate leather shavings waste. Shaved tanned grain sides are then "buffed" or sanded to create a very smooth surface. This generates a fine particulate leather buffing dust. Pieces of tanned leather are trimmed away to achieve the final leather shapes generating leather trimmings.

During other finishing steps dyes and colors are applied, the leather is lubricated, retanned with organic chemicals, and otherwise processed to make finished colored leather products (clothing, automobile and furniture coverings, etc.). Some waste dyes, organic solvents, etc., enter the waste stream at this point. Most tanneries have ceased use of Pb pigments. This has sharply lowered Pb levels in their wastes.

Nature of Leather Manufacturing Wastes

The Cr, Pb, and sulfide levels in the many possible leather manufacturing wastes have been described (29, 35, 68). Chromium ranged from 2,200 to 21,000 ppm wet weight, and Pb from 40 to 724 ppm. During a site visit we obtained samples of solid wastes from a modern tannery. Analyses showed low Cd, Pb, Zn, Cu, and Ni in all wastes, as was reported by Thorstenen and Shah (77). Segregation of Cr-rich wastewaters for separate treatment has kept the Cr level in waste streams other than Cr recycle sludge relatively low. The wastewater treatment sludge was high on Mn from use of Mn^{2+} to catalyze sulfide oxidation, and this may merit study.

Uses of Leather Wastes

Technology has been developed to utilize some tannery wastes. Leather trimming, shaving, and buffing wastes (collectively called leather tankage) are essentially pieces of Cr tanned leather, or fairly pure protein containing about 11% N and 1% Cr. Because of the protein-N, these wastes are now used as a feed ingredient or organic-N fertilizer.

Use as Feed --In response to a petition, FDA developed rules for use of hydrolyzed leather meal as an approved feed ingredient for swine (6). It may contain no more than 2.75% Cr, and may not comprise more than 1% of the mixed feed. Other feed uses will require new petitions.

Results of feeding trials with leather tankage have been reported by numerous researchers (23, 39, 46, 62, 67, 83). In general, they found that steaming or acid hydrolysis raises its protein equivalent value, and that the N is used in a manner similar to urea by sheep. No toxicity has been reported. Reduced rates of gain may result if the hydrolyzed leather meal is used to replace too high a proportion of the total protein in a feed.

Use as a Fertilizer --Because tannery wastes contain organic N in the form of the protein collagen, they have been tested for use as fertilizers. Leather tankage normally contains about 11% N. A process was developed to react leather tankage with urea and formaldehyde to produce a higher N analysis fertilizer. The product "Organiform", contains 22-24% N (9). The manufacturer has reported N release curves for this product in comparison with other commerical fertilizers. It contains no more than 2% Cr, and low levels of other heavy metals.

Use as Soil Conditioner/Fertilizer -- Many studies have been conducted on different leather manufacturing solid wastes and wastewater treatment sludges. Because research on land application of sewage sludges has pointed out several experimental difficulties in studying wastes, it would be useful to reevaluate the literature on land application of leather wastes.

When high application rates of unstabilized organic wastes are land-applied, the excessive BOD can cause anaerobic soil conditions and increase soluble organic compounds in the soil. Some of these are phytotoxic. Also, soluble salts can be phytotoxic until leached from the surface soil. Some soluble Cr may be found during anaerobic decomposition, but it is Cr^{3+} chelates. Studies using soluble metal salt additions to soils can not be used to estimate the effects on plants or ground water of applying wastes containing precipitated metals. This last point is especially relevant to Cr, since Cr^{3+} compounds and complexes are kinetically quite inert (1). When sludge Cr^{3+} precipitates equilibrate at pH 6 to 8, a quite stable insoluble Cr sludge forms. Study of soluble salts additions can lead to serious errors in estimating risks of Cr in leather manufacturing wastes.

Kick and Braun (44) reported studies on tannery sludge which was actually a Cr recycle sludge containing only 0.08% N and 32% Cr (dry weight). Research on this low volume inorganic waste is not useful toward understanding the potential effects on the environment of bulk organic tannery wastes containing only 0.3-3.0% Cr.

A number of conclusions can be drawn from the whole body of research on Cr-rich leather wastes, including study of tannery combined wastewater treatment sludges (47, 55, 56, 57, 82), POTW sludges produced largely from tannery wastewaters (2, 22, 24, 25, 26, 27, 38), and leather tankage (3, 5, 15, 48, 71, 72, 73).

1. The organic-N is apparently released more slowly than from other proteinaceous wastes because the Cr stabilizes the protein. Volk (82) estimates that about 10% of tannery wastewater treatment sludge N becomes crop available during the year of application.

2. These wastes seldom caused any phytotoxicity, especially when rates were limited to the N requirement of crops. Crops were somewhat enriched in Cr during the first crop year.

Leaching Chromate from Leather Waste Amended Soils --The critical remaining issue is leaching of Cr to groundwater. Chromate in groundwater may not exceed 50 ug/L (31, 33). If the immobile Cr^{3+} applied to soils in tannery wastes could be oxidized to the mobile chromate by soil MnO_2 (11), it seems possible that this could leach and contaminate ground water (35). However, Amacher and Baker (3) found that a soluble Cr-fulvic acid extracted from ground leather was not significantly oxidized by MnO_2. Chromate is rapidly reduced by soils to form insoluble chromic (13, 18, 76). Low concentrations of Cr are rapidly sorbed by soils (7). Soil water at 1 m depth was not increased in Cr by sewage sludge rich in tannery waste borne-Cr (24, 25). Water leaching from pots treated with ground leather at N-fertilizer rates was also not enriched in Cr (73).

Together, these studies support a model in which precipitated or chelated Cr is not readily oxidized by MnO_2, and that ground water will not be polluted by Cr from land-applied leather wastes if reasonable management is practiced regarding soil pH and rate of application. This hypothesis has not been proven conclusively by the present data since the lower redox potentials resulting from sludge application would more rapidly reduce any chromate formed back to chromic. Soils treated with leather wastes long ago should be evaluated since these are redox stabilized and would allow testing of worst case conditions. Field-moist, never-dried soils must be studied to avoid the errors identified by Bartlett and James (11).

In summary, most leather tanning in the U.S. uses chromium based processes. When tannery waste streams are segregated, only a few are high in Cr: the precipitated $Cr(OH)_3$ removed from used tanning solutions, and the leather trimmings, shavings, and buffing dust generated during transformation of tanned hides into finished leather. The precipitated Cr^{3+} waste has no practical use except to be recycled, and should not be considered for land application.

Leather wastes (tankage) have been converted to steamed leather meal, and are an approved swine feed ingredient. These wastes have been experimentally fed to swine, poultry, cattle, and sheep with no injury to the livestock. The protein is of low nutritional value (collagen).

Leather wastes (11%N) have also been treated by a urea-formaldehyde process to increase N content for use as a fertilizer. This is a commercial practice producing the 22-24% N product "Organiform." Land application of ground leather products supplies slow release nitrogen.

Chromium is somewhat increased in crops, at least during the first crop year after application of Cr-rich organic wastes. Chromium phytotoxicity has not resulted from land application of precipitated Cr^{3+}. Some other leather manufacturing wastewater treatment sludges have caused crop problems, but not demonstrably due to Cr. Many problems occur in pot studies with wastes because soluble salts are in excess, or inadequate fertilizers are applied for pot studies, etc.

A small amount of research has been conducted on leaching of Cr from soils treated with sewage sludge, tannery sludge, or chromate. Chromate in soil water at 1 m depth has not exceeded the 50 ug/L groundwater standard even when large amounts of Cr^{3+} bearing wastes are added. Often Cr in water at 1 m was unchanged by the surface applied Cr. Although soil MnO_2 can oxidize soluble Cr^{3+} to chromate, this appears to be environmentally irrelevant because Cr^{3+} has very low solubility at practical soil pH levels.

Research Needs for Land Treatment of Leather Manufacturing Wastes

Potential oxidation of chromic to chromate is important in environments rich in Cr^{3+}. More basic research is needed to assure that opportunities for environmental pollution by Cr are not ignored. The mechanisms of these reactions must be better understood. Chromium rich soils should be amended with MnO_2 to see whether environmentally stable chromic can be converted to chromate under some worst case conditions.

Land treatment sites freshly amended with tannery sludges will have lower oxidation potential than long-term well oxidized sites. These latter sites should be studied to see whether Cr^{3+} application can ever pollute groundwater with chromate. Economics of segregated treatment of tannery waste streams should be explored. Chromate leaching should be evaluated in relation to soil MnO_2, etc., since it is likely that most chromate leaching past the waste-amended surface soil will be reduced back to chromic and precipitated.

References

1. Allaway, W. H. 1977a. Soil and plant aspects of the cycling of chromium, molybdenum, and selenium. Proc. Intern. Conf. Heavy Metals in the Environment 1:35-47.

2. Alther, E. W. 1975. Chromium-containing sludge and chromium uptake by forage plants. Leder 26:175-178.

3. Amacher, M. C., and D. E. Baker. 1980. Kinetics of Cr oxidation by hydrous manganese oxides. Agron. Abstr. 1980:136.

4. Anderson, A. J., D. R. Meyer, and F. K. Mayer. 1973. Heavy metal toxicities: levels of nickel, cobalt, and chromium in the soil and plants associated with visual symptoms and variation in growth of an oat crop. Aust. J. Agric. Res. 24:557-571.

5. Andrzejewski, J. 1971. Effect of chromium fertilization on the yield of several plant species and on the chromium content of the soil (in Polish). Roczn. Nauk Rolnickzych A97:75-97.

6. Anonymous. 1967. Food additives permitted in the feed and drinking water of animals or for the treatment of food-producing animals. Fed. Reg. 32(157):11734.

7. Artiole, J., and W. H. Fuller. 1979. Effect of crushed limestone barriers on chromium attenuation in soils. J. Environ. Qual. 8:503-510.

8. Bailey, D. A., and F. E. Humphreys. 1967. The removal of sulphide from limeyard wastes by aeration. J. Soc. Leather Trades Chemists 51:154-172.

9. Baker, H. J., and Bros., Inc. 1972. Organiform LT. Product brochure. H. J. Baker Co., 360 Lexington Ave., New York, NY 10017

10. Bartlett, R. J., 1979. Oxidation-reduction status of aerated soils. Agron. Abstr. 1979:144.

11. Bartlett, R. J., and B. James. 1979. Behavior of chromium in soils: III. Oxidation. J. Environ. Qual. 8:31-35.

12. Bartlett, R. J., and J. M. Kimble. 1976a. Behavior of chromium in soils: I. Trivalent forms. J. Environ. Qual. 5:379-383.

13. Bartlett, R. J., and J. M. Kimble. 1976b. Behavior of chromium in soils: II. Hexavalent forms. J. Environ. Qual. 5:383-386.

14. Bauer, D. H., E. T. Conrad, and R. J. Lofy. 1977. Solid waste management practices in the leather tanning industry. J. Am. Leather Chem. Assoc. 72:270-280.

15. Berkowitz, J. B., S. E. Bysshe, B. E. Goodwin, J. C. Harris, D. B. Land, G. Leonardos, and S. A. Johnson. 1980. Field verification of land cultivation/refuse farming. p. 260-273. In D. Schulz (ed.) Proc. Sixth Ann. Res. Symp. on Disposal of Hazardous Waste. EPA-600-9-80-010.

16. Breeze, V. G. 1973. Land reclamation and river pollution problems in the Croal Valley caused by waste from chromate manufacture. J. Appl. Ecol. 10:513-525.

17. Cary, E. E., W. H. Allaway, and O. E. Olson. 1977a. Control of chromium concentration in food plants. 1. Absorption and translocation of chromium by plants. J. Agric. Food Chem. 25:300-304.

18. Cary, E. E., W. H. Allaway, and O. E. Olson. 1977b. Control of chromium concentration in food plants. 2. Chemistry of chromium in soils and its availability to plants. J. Agr. Food Chem. 25:305-309.

19. Chaney, R. L. 1980. Health risks associated with toxic metals in municipal sludge. pp. 59-83. In G. Bitton et al. (eds.) Sludge -- Health Risks of Land Application. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

20. Chaney, R. L., D. D. Kaufman, S. B. Hornick, J. F. Parr, L. J. Sikora, W. D. Burge, P. B. Marsh, G. B. Willson, and R. H. Fisher. 1981. Review of information relevant to land treatment of hazardous wastes. Draft Report to EPA-SHWRD.

21. Chapman, H. D. 1966. Diagnostic criteria for plants and soils. Univ. Calif., Division Agr. Sci., Riverside. 793pp.

22. Cunningham, J. D., D. R. Keeney, and J. A. Ryan. 1975. Yield and metal composition of corn and rye grown on sewage sludge-amended soil. J. Environ. Qual. 4:448-454.

23. Dilworth, B. C., and E. J. Day. 1970. Hydrolyzed leather meal in chick diets. Poult. Sci. 49:1090-1093.

24. Dowdy, R. H., C. E. Clapp, W. E. Larson, and D. R. Duncomb. 1979. Runoff and soil water quality as influenced by five years of sludge applications on a terraced watershed. Agron. Abstr. 1979:28.

25. Dowdy, R. H., C. E. Clapp, D. R. Duncomb, and W. E. Larson. 1980. Water quality of snowmelt runoff from sloping land receiving annual sewage sludge applications. pp. 11-15 In Proc. Nat. Conf. Municipal and Industrial Sludge Utilization and Disposal. Information Transfer, Inc., Silver Spring, MD.

26. Dowdy, R. H., and G. E. Ham. 1977. Soybean growth and elemental content as influenced by soil amendments of sewage sludge and heavy metals: Seedling studies. Agron. J. 69:300-303.

27. Dowdy, R. H., and W. E. Larson. 1975. The availability of sludge-borne metals to various vegetable crops. J. Environ. Qual. 4:278-282.

28. El-Bassam, N., P. Poelstra, and M. J. Frissel. 1975. Chromium and mercury in a soil after 80 years of treatment with urban sewage water. (In German). Z. Pflanzenern. Bodenk. 1975:309-316.

29. EPA. 1974. Development document for effluent limitations guidelines and new source performance standards for the leather tanning and finishing point source category. EPA-440/1-74-016-a. 158 pp.

30. EPA. 1979. Criteria for classification of solid waste disposal facilities and practices. Federal Register 44(179):53438-53464.

31. EPA. 1980a. Hazardous waste management system: Identification and listing of hazardous waste. Federal Register 95(98):33084-33133.

32. EPA. 1980b. Hazardous waste management system: Standards for owners and operators of hazardous waste treatment, storage, and disposal facilities. Federal Register 45(98):33154-33258.

33. EPA. 1980c. Hazardous waste management system: Identification and listing of hazardous wastes. Fed. Reg. 45(212):72029-72034.

34. EPA. 1980d. Hazardous waste management system: Identification and listing of hazardous wastes. Fed. Reg. 45(212):72037-72039.

35. EPA. 1980e. Listing background document: Leather tanning and finishing industry. Supports Appendix 7 in EPA (1980a). On file in Docket 3001 at EPA.

36. Gemmel, R. P. 1973. Revegetation of derelict land polluted by a chromate smelter. 1: Chemical factors causing substrate toxicity in chromate smelter waste. Environ. Pollut. 5:181-197.

37. Gemmell, R. P. 1974. Revegetation of derelict land polluted by a chromate smelter. 2: Techniques of revegetation of chromate smelter waste. Environ. Pollut. 6:31-37.

38. Grove, J. H., and B. G. Ellis. 1980. Extractable chromium as related to soil pH and applied chromium. Soil Sci. Soc. Am. J. 44:238-242.

39. Gruhn, K., and H. Luedke. 1972. Use of hydrolyzed chrome leather waste in pig feeding and the content of chromium in flesh, liver, kidneys, and hair (in German). Arch. Tierernaehr. 22:113-124.

40. Hafez, A. A. R., H. M. Reisenauer, and P. R. Stout. 1979. The solubility and plant uptake of chromium from heated soils. Commun. Soil Sci. Plant Anal. 10:1261-1270.

41. Hauck, R. A. 1972. Report on methods of chromium recovery and reuse from spent chrome tan liquor. J. Am. Leather Chem. Assoc. 67:722-430.

42. Huffman, E. W. D., Jr. and W. H. Allaway. 1973. Growth of plants in solution culture containing low levels of chromium. Plant Physiol. 52:72-75.

43. Irwin, M. I., and E. W. Crampton. 1951. The use of chromic oxide as an index material in digestion trials with human subjects. J. Nutr. 43:77-85.

44. Kick, H., and B. Braun. 1977. The effect of chromium containing tannery sludges on the growth and the uptake of chromium by different crops (in German). Landwirtsch. Forsch. 30:160-173.

45. Kienholz, E. W. 1980. Effect of toxic chemicals present in sewage sludge on animal health. pp. 153-171. *In* G. Bitton et al. (eds.) *Sludge--Health Risks of Land Application*. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

46. Knowlton, P. H., W. H. Hoover, C. J. Sniffen, C. S. Thompson, and P. C. Belyea. 1976. Hydrolyzed leather scrap as a protein source for ruminants. J. Anim. Sci. 43:1095-1103.

47. Koc, J. 1979. Effect of the temperature, moisture content in soil, and additions of fertilizers on the decomposition of tannery sludges (in Polish). Rocz. Glebozn. 30:73-83.

48. Kravchenko, S. N. 1979. Effect of leather waste on the yield and quality of some vegetable crops (in Russian). Nauchnye Trudy Ukr. S.-Kr. Akad. 228:62-65.

49. Lyon, G. L., R. R. Brooks, and P. J. Peterson. 1969. Chromium-51 distribution in tissues and extracts of *Leptospermum scoparium* J. R. et G. *Forst. (Myrtaceae)*. Planta 88:282-287.

50. Lyon, G. L., R. R. Brooks, P. J. Peterson, and G. W. Butler. 1968. Trace elements in a New Zealand serpentine flora. Plant Soil 29:225-240.

51. Lyon, G. L., R. R. Brooks, P. J. Peterson, and G. W. Butler. 1970. Some trace elements in plants from serpentine soils. N. Z. J. Sci. 13:133-139.

52. Lyon, G. L., P. J. Peterson, and R. R. Brooks. 1969. Chromium-51 transport in the xylem sap of *Leptospermum scoparium* J. R. et G. *Forst. (Myrtaceae)*. N. Z. J. Sci. 12:541-545.

53. Lyon, G. L., P. J. Peterson, R. R. Brooks, and G. W. Butler. 1971. Calcium, magnesium, and trace elements in a New Zealand serpentine flora. J. Ecol. 59:421-429.

54. Maire, M. S. 1977. A comparison of tannery chrome recovery systems. J. Am. Leather Chem. Assoc. 72:404-418.

55. Mazur, T., and J. Koc. 1976a. The fertilizing value of tannery sludge. II. Effect of fertilization with tannery sludges on the crop (in Polish). Rocz. Glebozn. 27:113-122.

56. Mazur, T., and J. Koc. 1976b. The fertilizing value of tannery sludge. III. Effect of fertilization with tannery sludges on the chemical composition of plants (in Polish). Rocz. Glebozn. 27:123-135.

57. Mazur, T., and J. Koc. 1980. The fertilizing value of tannery sludges. p. 328-338. *In* Handbook of organic waste conversions. Van Nostrand-Reinhold, New York.

58. McLellan, J. S., P. R. Flanagan, M. J. Chamberlain, and L. S. Valberg. 1978. Measurement of dietary cadmium absorption in humans. J. Toxicol. Environ. Health 4:131-138.

59. Mertz, W. 1969. Chromium occurrence and functions in biological systems. Physiol. Rev. 49:165-239.

60. Mortvedt, J. J., and P. M. Giordano. 1975. Response of corn to zinc and chromium in municipal wastes applied to soil. J. Environ. Qual. 4:170-174.

61. NRC. 1980. Mineral Tolerance of Domestic Animals. National Academy of Sciences, Washington, D.C. 577pp.

62. Otevrelova, K., and M. Mackova. 1977. Tanning waste in feeds for fur animals. 1. Hydrolytic treatment of different types of waste to increase digestibility (in Czech.). Sbornik Vedeckych Praci Vyzkumneho Ustavu Vyzivy Zvirat, Pohorelice 11:41-48.

63. Petrilli, F. L., and S. deFlora. 1977. Toxicity and mutagenicity of hexavalent chromium on *Salmonella typhimurium*. Appl. Environ. Microbiol. 33:805-809.

64. Pierce, R., and T. C. Thornstenen. 1976. Recycling of chrome tanning liquors. J. Am. Leather Chem. Assoc. 71:161-164.

65. Proctor, J., and S. R. J. Woodell. 1975. The ecology of serpentine soils. Adv. Ecol. Res. 9:255-366.

66. Raleigh, R. J., R. J. Kartchner, and L. R. Rittenhouse. 1980. Chromic oxide in range nutrition studies. Oregon State Univ. Agr. Exp. Sta. Bull. 641:1-41.

67. Salimbaev, S. 1979. Use of tannery shavings for fattening pigs (in Russian). Zhivotnovodstvo 8:60-61.

68. SCS Engineers, Inc. 1976. Assessment of industrial hazardous waste practices - Leather tanning and finishing industry. NTIS # PB 261-018.

69. Shewry, P. R., and P. J. Peterson. 1974. The uptake and transport of chromium by barley seedlings (*Hordeum vulgare* L.). J. Exp. Bot. 25:785-797.

70. Shewry, P. R., and P. J. Peterson. 1976. Distribution of chronium and nickel in plants and soil from serpentine and other sites. J. Ecol. 64:195-212.

71. Shivas, S. A. J. 1980a. Factors affecting the oxidation state of chromium disposed in tannery wastes. J. Am. Leather Chem. Assoc. 75:42-48.

72. Shivas, S. A. J. 1980b. The effects of trivalent chromium from tannery wastes on plants. J. Am. Leather Chem. Assoc. 75:288-299.

73. Silva, S., and B. Beghi. 1979. Problems inherent in the use of organic fertilizers containing chromium. Ann. Della Fac. Agr. Univ. Cath. Sacro Cuore 19(1):31-47.

74. Skeffington, R. A., P. R. Shewry, and P. J. Peterson. 1976. Chromium uptake and transport in barley seedlings (*Hordeum vulgare* L.). Planta 132:209-214.

75. Slater, J. P., and H. M. Reisenauer. 1979. Toxicity of Cr(III) and Cr(VI) added to soils. Agron. Abstr. 1979:38.

76. Taylor, F. G., Jr. 1980. Chromated cooling tower drift and the terrestrial environment: A review. Nuclear Safety 21:495-508.

77. Thorstenen, T. C., and M. Shah. 1979. Technical and economic aspects of tannery sludge as a fertilizer. J. Am. Leather Chem. Assoc. 74:14-23.

78. Toepfer, E. W., W. Mertz, M. M. Polansky, E. E. Roginski, and W. R. Wolf. 1977. Preparation of chromium-containing material of glucose tolerance factor activity from brewer's yeast extracts and by synthesis. J. Agr. Food Chem. 25:162-166.

79. Towill, L. E., C. R. Shriner, J. S. Drury, A. S. Hammons, J. W. Holleman, and J. O. Pierce. 1978, Reviews of the environmental effects of pollutants: III. Chromium. EPA-600/1-78-023.

80. Turner, M. A. and R. H. Rust. 1971. Effects of chromium on growth and mineral nutrition of soybeans. Soil Sci. Soc. Am. Proc. 35:755-758.

81. Underwood, E. J. 1977. Trace Elements in Human and Animal Nutrition. 4th Ed. Academic Press, New York. 545pp.

82. Volk, V. V. 1980. Department of Agronomy, Oregon State University, Corvallis, OR. Personal communication.

83. Waldrup, P. W., C. M. Hillard, W. W. Abbott, and L. W. Luther. 1970. Hydrolyzed leather meal in broiler diets. Poult. Sci. 49:1259-1264.

84. Whitby, L. G., and D. Lang. 1960. Experience with the chromic oxide method of fecal marking in metabolic balance investigations on humans. J. Clin. Invest. 39:854.

85. Wild, H. 1974. Indigenous plants and chromium in Rhodesia. Kirkia 9:233-241.

ASSESSMENT OF HYDROCARBON EMISSIONS FROM LANDTREATMENT OF OILY SLUDGES

Robert G. Wetherold
Radian Corporation
8501 Mo-Pac Boulevard
Austin, Texas 78758

Donald D. Rosebrook
Radian Corporation
8501 Mo-Pac Boulevard
Austin, Texas 78758

E. W. Cunningham
Standard Oil Company (Ohio)
Midland Building
Cleveland, Ohio 44115

The first phase of a program to assess the atmospheric emissions from the landfarming of refinery oily sludges has been recently completed. This study is jointly funded by the American Petroleum Institute and the U.S. Environmental Protection Agency. The first phase of this study was intended to characterize refinery oily sludges and to examine the effects of a number of parameters on the mass and rate of fugitive hydrocarbon emissions from the landfarming of refinery oily sludges. A small laboratory apparatus was developed to simulate some landfarming operations. All of the studies reported in this paper were conducted in this enclosed landfarm simulator in which the major important variables could be controlled.

The variables which were studied included sludge type, sludge volatility, soil moisture content, wind speed, relative humidity, air temperature, soil temperature, sludge loading on soil, and sludge application technique.

Important parameters affecting emission rates and total hydrocarbon mass emissions were found to include sludge volatility, sludge loading on soil, application method (surface or subsurface), and soil moisture content (and/or porosity).

Introduction

Oily sludges, which are generated in various petroleum refinery operations, must be disposed of in an environmentally acceptable manner. Provisions of the Resource Conservation and Recovery Act of 1976 restrict the available options for disposal of this waste. One accepted method of disposal for refinery oily sludge that appears to be economically attractive is landfarming. This technique has been practiced in some refineries for several years, but it has attracted much more interest in recent years. Along with this growing interest, several studies have been initiated to investigate landfarming techniques.

In 1980, the American Petroleum Institute (API) and the Environmental Protection Agency (EPA) jointly funded a study to assess the atmospheric emissions from the landfarming of refinery oil sludges. The program was carried out by Radian Corporation.

The objectives of the study were:

- to determine the magnitude of hydrocarbon emissions from landfarming operations with refinery oil sludges,
- to identify those sludge characteristics and landfarming parameters which have the greatest influence on the magnitude of hydrocarbon emissions,
- to develop methods of characterizing sludges, and
- to develop a method to predict the emissions from landfarming operations from sludge characteristics and operating parameters.

The first phase of this program has recently been completed. Sludge characterization tests and laboratory simulations of landfarming operations were carried out in this phase. This paper presents some of the more important results obtained in the study.

Experimental Procedures

Sludges were characterized by both physical and chemical testing, and a stripping test was developed to provide a measure of the sludge volatility. A landfarming simulation system was developed in the laboratory to evaluate the emissions under varying landfarming conditions.

The oily sludges were subjected to the following physical tests:

- total solids,
- total volatile solids,
- total suspended solids,
- total volatile suspended solids,
- weight loss during heating, and
- centrifugation.

The chemical characterization tests performed on the sludge included:

- oil and grease content of the sludges, and
- gas chromatography-mass spectrometry for volatile organic species in the sludges and soils.

The oil and grease content of the sludges was estimated by two separate methods. In the gravimetric method, oil and grease is extracted from the sludge sample with Freon. The solvent is then evaporated. The remaining residue is considered to be oil and grease.

An infrared procedure was also used to estimate the oil and grease content of the sludges. The sludge is extracted with Freon, but the Freon is not evaporated. Instead, infrared absorption measurements are made which correspond to the concentrations of the hydrocarbons present in the solvent. The absorbance values are compared to those obtained with a reference oil composed of isooctane, hexadecane, and benzene.

Sludge samples were subjected to a stripping test in an effort to obtain a quantitative measure of their relative volatility. In this test a Bellar tube and a Byron Instruments Model 301C Total Hydrocarbon Analyzer (THC) were used. A schematic diagram of the apparatus is shown in Figure 1. The Bellar tube was filled with 25 ml of water and a small volume of sludge was added. Nitrogen was purged at a constant measured rate through the water-sludge mixture. The nitrogen stream from the Bellar tube was analyzed for hydrocarbons with the Byron 301C THC.

The THC can perform an analysis every four minutes. The stripping was continued for at least 80 minutes.

The landfarming simulation device developed in this study is shown in Figure 2.

The soil chamber provides one square foot of soil surface area. Two different plexiglass soil chambers were used which provided for either 4 inch or 14 inch soil depths. Each chamber had 4 inches of head space above the soil. Incoming air was heated as desired by a 1,650 watt heater placed in front of the air intake to the chamber. Air temperature and relative humidity were monitored in the exit duct.

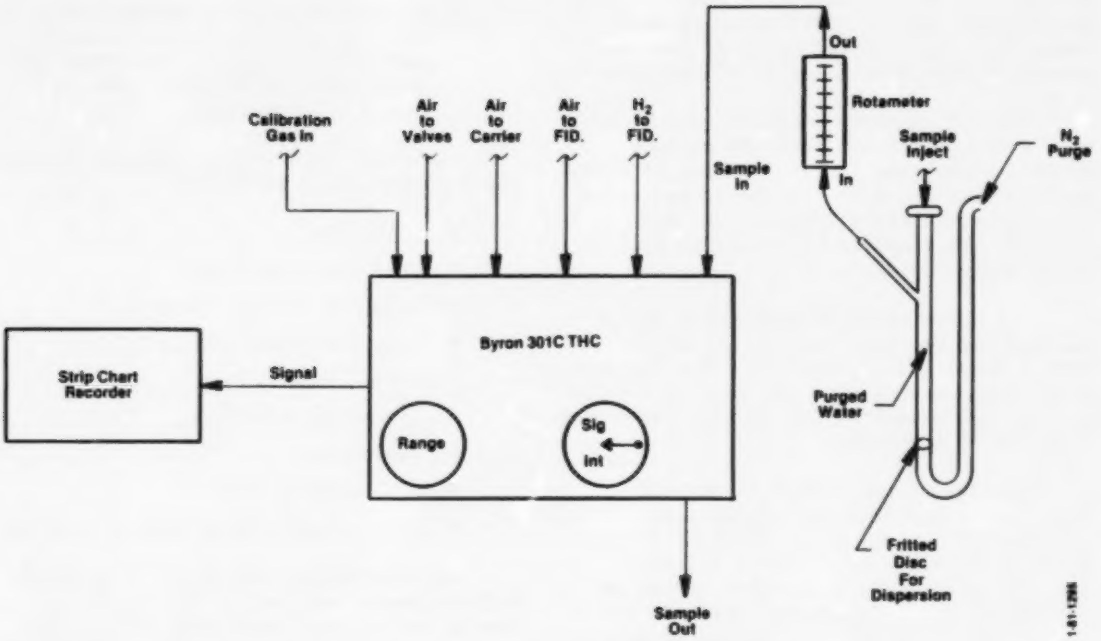

Calibration Gas In
Air to Valves
Air to Carrier
Air to FID.
H_2 to FID.
Sample In
Out
Rotameter
In
Sample Inject
N_2 Purge
Strip Chart Recorder
Signal
Byron 301C THC
Range
Sig
Int
Purged Water
Fritted Disc For Dispersion
Sample Out
1-81-1296

Figure 1. Stripping Test Apparatus

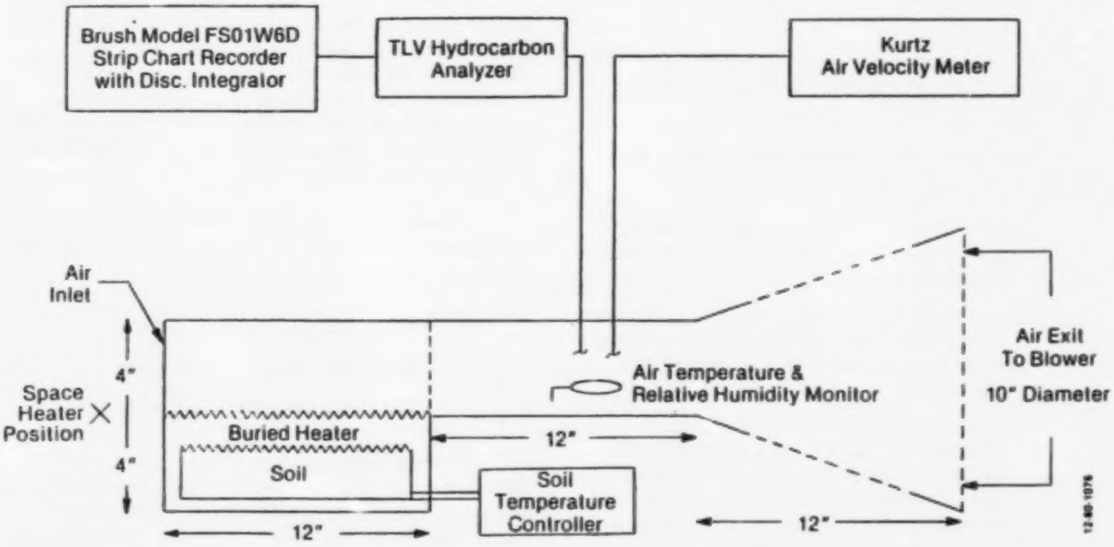

Brush Model FS01W6D Strip Chart Recorder with Disc. Integrator
TLV Hydrocarbon Analyzer
Kurtz Air Velocity Meter
Air Inlet
4"
Space Heater Position
4"
Buried Heater
Soil
12"
Air Temperature & Relative Humidity Monitor
12"
Soil Temperature Controller
12"
Air Exit To Blower
10" Diameter
12-80-1076

Figure 2. Landfarm Simulation Apparatus

Soil temperature was varied by means of a heater buried one inch below the soil surface and controlled with a feedback temperature controller. Soil moisture and temperature were varied manually and monitored with a Soiltest MC300B analyzer

The air velocity could be controlled with a Dayton 2C939A, 2000 CFM exhaust blower in the exit duct. A series of holes in this duct could be covered or uncovered to achieve the desired velocity. Air velocity was measured with a Kurtz (hot wire) air velocity meter.

The hydrocarbon concentration in the air leaving the soil chamber was monitored with a Bacharach TLV Sniffer. The Sniffer probe was inserted into the exit ducting at a point approximately six inches downstream from the soil chamber.

Samples of the sludge to be studied were preweighed into one-gallon jugs. Attached to the jug was a piece of Teflon tubing leading to a 12 inch × 1/2 inch piece of plexiglass tube which served as a spreader bar. The plexiglass tube had a number of 1/8 inch holes drilled in it to allow spreading of the sludge. Subsurface injection was simulated by repeated insertion of the wand from a hand pressurized garden sprayer.

Tilling was accomplished manually with a small, short-handled four-tined garden hoe.

A typical simulation run using the above apparatus was conducted as follows:

1. The heaters (air and soil) were turned on and set for the desired temperatures.
2. The exhaust blower was started and the flow rate through the duct was adjusted to attain the desired velocity.
3. The Bacharach TLV Sniffer was turned on and the instrument and recorder were zeroed on ambient air in what was a hydrocarbon-free environment. Instrument response was checked with methane (533 ppm).
4. After recording a background hydrocarbon level, the preweighed amount of sludge was spread over the soil surface (or injected, as the case may be). This operation required somewhat less than 60 seconds.
5. Hydrocarbon concentration levels in the air (leaving the soil chamber) and disc-integrated peak areas were monitored continuously from the start of spreading.

Variables that were considered in this phase of the study included:

- soil type,
- air/soil temperature,
- moisture content of soil,
- relative humidity,
- sludge volatility,
- spreading technique,
- wind speed,
- soil loading, and
- sludge temperature during spreading.

In landfarming simulation experiments, each parameter was varied independently from a set of base conditions to a higher or lower value. In some cases, additional values were tested to more clearly define the effects of a particular parameter.

A total of 24 experiments were run in which sludges were applied to soils in the laboratory simulation of landfarming. The matrix of experiments and experimental conditions is presented in Table 1. Two soils, Soil S and Soil T, were used in the simulations. These soils were taken from operating refinery landfarms.

Three oily sludges were obtained from refineries engaged in landfarming. These sludges are identified as:

S1 - storage tank bottoms
S3 - API separator sludge
T - API separator sludge

It was necessary to calibrate the TLV Sniffer disc integrator to get quantitative results from the landfarming simulation experiments. This was done by fitting the soil box with a false bottom at the normal soil level. The modified soil box was placed on a Mettler P4400 balance. Sludge S1 samples were placed on the false bottom of the soil box. The conditions were

TABLE 1. MATRIX OF EXPERIMENTAL CONDITIONS FOR LANDFARM SIMULATION RUNS

Run No.	Waste Material	Waste Loading (lb/ft^2)	Soil Type	Soil Moisture (wt%)	Soil/Air Temperature (°F/°F)	Air Velocity (mph)	Relative Humidity (%)	Spreading Mechanism	Remarks
1	Hexane	1.0	None	NA	NA/100	3	Amb*	Pour	Pure hexane - no soil
2	Hexane	1.0	S	10.7	120/100	3	Amb*	Surface	Pure hexane with soil
3	Gasoline	1.0	None	NA	NA/100	3	Amb*	Pour	Pure gasoline-no soil
4	Gasoline	1.0	S	10.7	120/100	3	Amb*	Surface	Pure gasoline with soil
5	S1	2.5	None	NA	NA/100	3	Amb*	Pour	Sludge 1 with no soil
6	S1	2.5	S	10.7	120/100	3	Amb*	Surface	Base case
7	S1	2.5	S	10.7	120/100	3	Amb*	Surface	Repeat of base case
8	S1	2.5	S	10.7	120/100	1	Amb*	Surface	Reduced air velocity
9	S1	2.5	S	10.7	100/80	3	40	Surface	Reduced soil/air temperature
10	S1	1.0	S	10.7	120/100	3	Amb*	Surface	Reduced soil loading
11	S1	1.0	S	10.7	120/100	3	Amb*	Surface	Repeat of Run 10
12	S1	2.5	T	4.7	120/100	3	Amb*	Surface	Used Soil T
13	S1	2.5	S	20.7	120/100	3	Amb*	Surface	Increased soil moisture
14	S1	2.5	S	10.7	120/100	3	75	Surface	Increased relative humidity
15	T	2.5	S	10.7	120/100	3	Amb*	Surface	Used sludge T
16	S1	2.5	S	10.7	120/100	3	Amb*	Surface	Base case with deeper (14") soil box
17	S1	4.0	S	10.7	120/100	3	Amb*	Surface	Increased soil loading
18	S1	0.5	S	10.7	120/100	3	Amb*	Surface	Lowest soil loading
19	S1	2.5	S	10.7	120/100	3	Amb*	Surface	Heat sludge to 140°F before application
20	S3	1.0	S	10.7	120/100	3	Amb*	Surface	Sludge S3 at low loading
21	S3	2.5	S	10.7	120/100	3	Amb*	Surface	Sludge S3 at base case loading
22	S3	4.0	S	10.7	120/100	3	Amb*	Surface	Sludge S3 at increased loading
23	S3	1.0	T	4.7	120/100	3	Amb*	Surface	Sludge S3 with soil T-low loading
24	S3	4.0	T	4.7	120/100	3	Amb*	Surface	Sludge S3 with soil T-high loading
25	S3	2.5+	S	10.7	120/100	3	Amb*	Surface	Spike sludge with 0.5 lb of gas
26	S3	2.5+	S	10.7	120/100	3	Amb*	Surface	Spike sludge with 1.5 lb of gas
27	S3	2.5+	S	10.7	120/100	3	Amb*	Surface	Spike sludge with 1.5 lb of H_2O
28	S1	2.5	S	10.7	120/100	3	Amb*	Subsurface	Till soil after spreading
29	S1	2.5	S	10.7	120/100	3	Amb*	Subsurface	Use deeper injection

*Amb = ambient humidity was typically 50% at room temperature but measured <<30% at 100°F.

adjusted to the base case conditions (Runs 6 and 7). Then the weight loss due to vaporization was measured as a function of time. The integrated area under the TLV Sniffer recorder curve was also monitored as a function of time. From these values, a calibration factor which relates weight loss to integrated area can be estimated.

Results

The three sludge samples were quite different from one another in their physical characteristics. Sludge S1 contained approximately 92 percent oil (by weight). Sludge S3 contained approximately 20 percent oil, while only 10 percent of Sludge T consisted of oil.

There was also a marked difference in their apparent volatility. Results of stripping tests on samples of the three sludges are shown in Figure 3. Sludge S1 is the most volatile while Sludge T is the least.

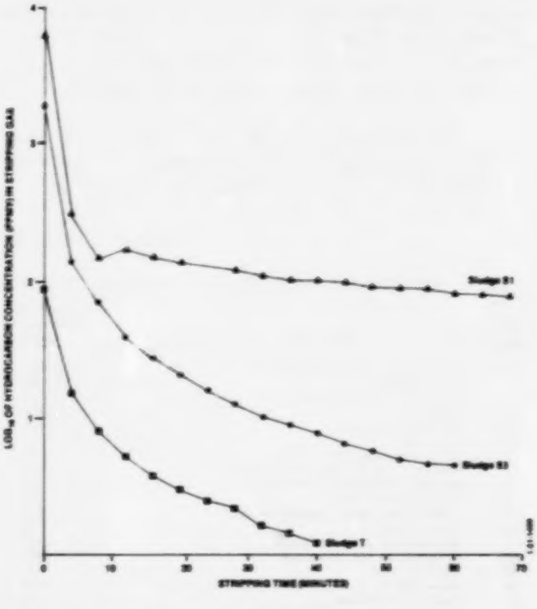


Figure 3. Concentration of Hydrocarbons in Purge Gas During Stripping Tests

In the course of the landfarming simulation experiments, a concentration-time plot, such as that shown in Figure 4, was generated for the hydrocarbon concentration in the air flowing across the sludge-laden soil. In almost every case there was a very rapid rise in hydrocarbon concentration, usually reaching a maximum within a minute or two of the start of the spreading operation. An equally precipitous decline from the maximum and a slow approach to zero (laboratory ambient air) usually followed. Generally, the concentration declined to about 1-2 ppm in about 30-60 minutes from the time of spreading.

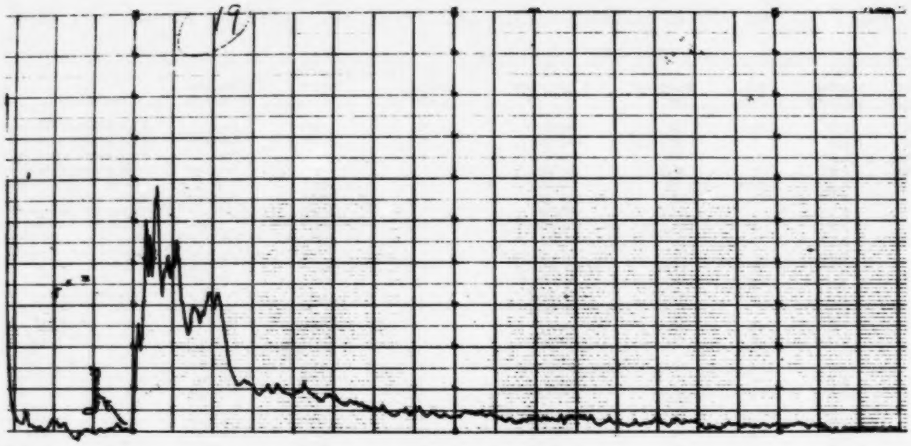


Figure 4. Typical Chart Trace from THC Monitor

The results of the 29 landfarming simulation experiments are presented in Table 2. The maximum hydrocarbon concentration, and the integrated area under the concentration-time trace at six minutes and 30 minutes from spreading are given for each run. The area is expressed in arbitrary (but consistent) area units.

The results of the calibration of the landfarming simulation apparatus are shown in Figure 5. The calibration factor of 9.85 area units/gram was used to estimate the weight loss of hydrocarbon during the landfarming simulations. The weight losses were calculated from the 30-minute integrated time-hydrocarbon concentration curve, with the following assumptions:

- The response of the TLV Sniffer to sludge S1 vapors during the simulation tests was linear and equal to that determined in the calibration.

TABLE 2. RESULTS OF SIMULATION RUNS

Run No.	Variable[1]	Maximum Hydrocarbon (ppm)	Integrated Area In 6 Min.	Integrated Area In 30 min.	Remarks
1	Pure hexane (false bottom)	> 10,000	2,460	7,980	8580 area at dryness
2	Pure hexane	> 10,000	3,900	5,500	
3	Gasoline (false bottom)	> 5,000	670	1,810	2400 area at zero hydrocarbons
4	Gasoline	> 10,000	1,750	2,470	
5	S1 (false bottom)	400	43	342	
6	Base case	215	21	78	
7	Base case (repeat)	200	22	62	
8	Air velocity decreased to 1 mph	310	57	231	
9	Air/soil temperature decreased	260	23	53	
10	Loading decreased	325	49	143	
11	Loading decreased (repeat of 10)	200	31	136	
12	Soil T used	485	86	230	
13	Moisture in soil increased	> 500	85	263	
14	Moisture in air increased	> 500	68	116	
15	Waste T used	35	1	1	
16	Base Case in a deeper box	350	27	71	
17	Loading increased	425	33	81	
18	Loading decreased drastically	250	31	61	
19	Waste heated before spreading	350	45	74	
20	Waste S3 at low loading	23	4	10	
21	Waste S3 used	15	1.5	5	
22	Waste S3 at high loading	25	4	16	
23	Waste S3 low load on T soil	17	2	5	
24	Waste S3 high load on T soil	34	4	12	
25	Waste S3 with low gas spike	7,000	480	760	
26	Waste S3 with high gas spike	> 10,000	760	1,360	
27	Waste S3 cut with water	25	5	8	
28	Subsurface injection	300	17	114	
28A	Tilling of 28	375	29	68	Tilled 80 min. after spreading
29	Subsurface deep injection	0	0	0	
29A		225	15	15	Tilled 4 days after spreading
29B		50	3	3	Tilled 6 days after spreading

[1] Variable changes from the base case conditions of Runs 6 and 7. All other variables remained as in Runs 6 and 7.

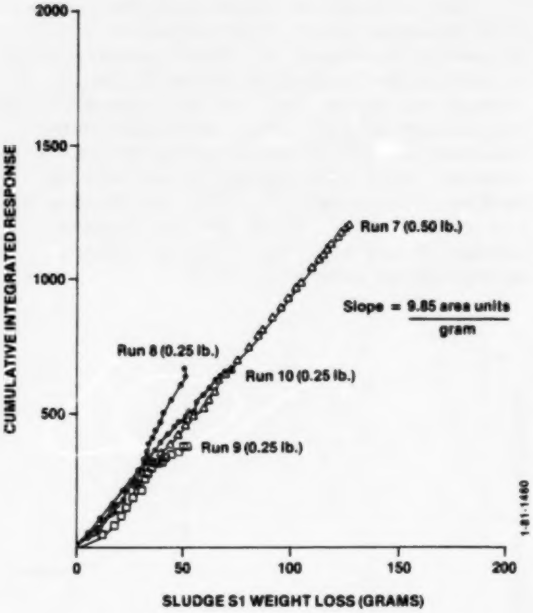


Figure 5. Calibration Factor for Sludge S1 Vaporization in Landfarming simulator

- The response of the TLV Sniffer to sludges S3 and T vapors is the same as that for sludge S1 vapors.

The results are shown in Table 3, and they indicate that from 0.5 to 3.2 percent of the total applied sludge S1 is lost in the first 30 minutes after application. Slightly larger percent losses relative to the total applied oil are incurred. Only 0.07 to 0.22 percent of the total weight of sludge S3 is emitted in 30 minutes, but this represents from 0.22 to 1.1 percent of the oil applied. Sludge T loses only 0.09 percent of the applied oil and an order-of-magnitude less of the total applied weight in 30 minutes. Thus, the most volatile sludge, sludge S1, as determined from the stripping test, emits the most hydrocarbons. Conversely, the least volatile sludge, sludge T, emits the least material.

The effect of volatility on emissions is further illustrated in Figure 6. The emissions are proportional to the relative response of the TLV Sniffer. The relative responses at the maximum concentration and for the 6-minute and 30 minuted cumulative response (area) are shown. The behavior of the three sludges (S1, S3, and T) during the landfarming simulation indicates the

TABLE 3. ESTIMATED EMISSIONS FROM SLUDGE APPLIED TO SOIL IN LANDFARMING SIMULATION TESTS

Run/Sludge	Area 30	Grams Volatilized*	Weight Sludge Applied, g	% Total Sludge Volatilized	Weight Oil Applied	% Volatilized
6/S1	78	7.9	1135	0.70	1044	0.75
7/S1	62	6.3	1135	0.56	1044	0.60
9/S1	53	5.4	1135	0.48	1044	0.52
10/S1	143	14.5	454	3.2	418	3.5
11/S1	136	13.8	454	3.0	1044	1.3
12/S1	230	23.3	1135	2.1	1044	2.2
13/S1	263	26.7	1135	2.4	1044	2.6
14/S1	116	11.8	1135	1.0	1044	1.1
15/T	1	0.10	1135	0.009	114	0.088
16/S1	71	7.2	1135	0.63	1044	0.69
17/S1	81	8.2	1816	0.45	1671	0.49
18/S1	61	6.2	227	2.7	209	3.0
19/S1	74	7.5	1135	0.66	1044	0.72
20/S3	10	1.0	454	0.22	91	1.1
21/S3	5	0.51	1135	0.045	227	0.22
22/S3	16	1.6	1816	0.088	363	0.44
23/S3	5	.51	454	.11	91	0.56
24/S3	12	1.2	1816	0.066	363	0.33
27/S3	8	.81	1135	0.071	227	0.36

*Based on response factor given in Figure 5 higher emissions of the more volatile sludge (S1).

As a further test of the volatility effect, 0.5 and 1.5 pounds (lbs) of gasoline were added to 2.5 lbs of sludge S3 and the mixtures were applied to the soil in the simulator. The results of these tests are also shown in Figure 6. The emission rates of the mixtures were much higher than that of the unadulterated sludge. In addition, the 6-minute and 30 minute cumulative responses (areas) indicated an increase in emissions with increased amounts of added gasoline.

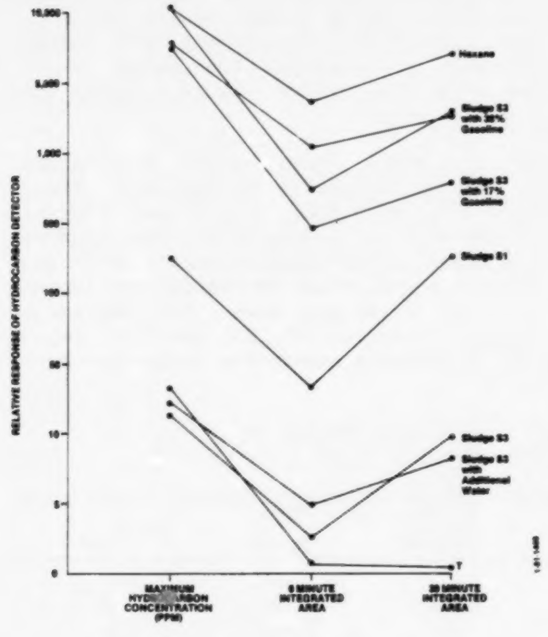


Figure 6. Effect of Volatility

In another test, 1.5 lbs of water were added to 2.5 lbs of sludge, and the mixture applied to the soil surface in the simulator. As shown in Figure 6, there was virtually no effect of the additional water on the emission rate.

The amount of sludge applied to the soil surface (loading) was varied to discern any effect on the emissions rate. Variable loadings were examined only for sludges S1 and S3. The emissions from sludge T were so low at a loading of 2.5 lb/ft² that any effect of loading would very likely be undetectable.

The effects of loading on the cumulative response after 30 minutes are presented in Figure 7. There appears to be a worst-case loading in terms of pounds of sludge per square foot of soil particularly for sludge S1 (all other variables being constant). Within the loading ranges studied, this same phenomena was not as evident for sludge S3. This may be due to the effect of the water in the sludges. Sludge S1 contains virtually no water; sludge S3 is primarily water.

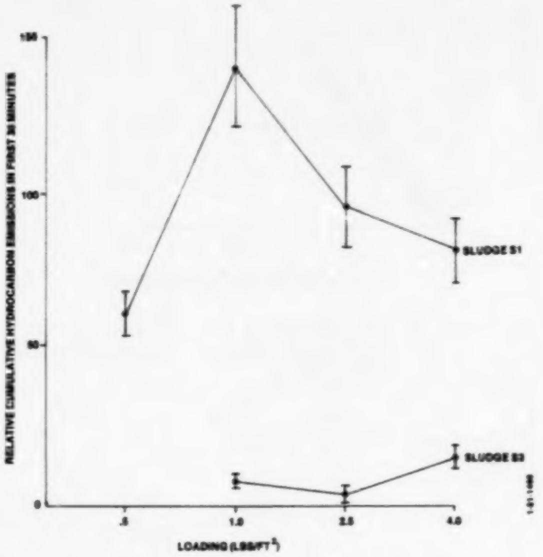


Figure 7. Hydrocarbon Emissions as a Function of Soil Loading

Two subsurface injection experiments were carried out, and they produced quite different results. In the first case (Run 28) injection was performed at a shallow depth (~ 3-4 inches) and some sludge actually bubbled to the surface. The emissions were relatively high during the initial application and during the tilling which was done 80 minutes after application (see Table 2).

A second subsurface injection experiment was performed in which the sludge was injected at a deeper level (~6 inches) in the soil. No sludge appeared on the surface of the soil. There were no detectable emissions during or after the sludge injection. The soil was tilled after four days and again after six days. Some hydrocarbons were detected in the air at the time

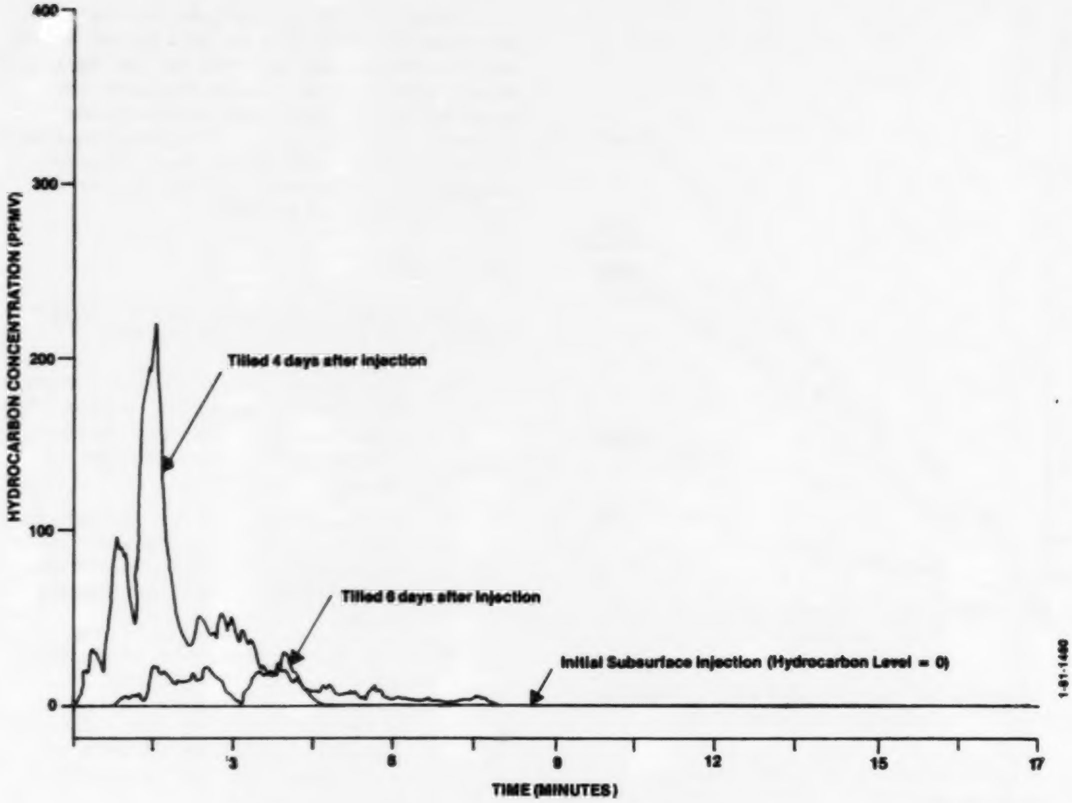


Figure 8. Effect of Resting Time Before Tilling on Emissions After Subsurface Injection.

of tilling. Figure 8 shows the chart tracings for these three measurements. There can be little doubt from these experiments that a substantial overall emission reduction can be achieved by subsurface injection and a reasonable waiting period before tilling.

Figure 9 shows the effects of various other parameters on the relative magnitude of emissions from the landfarming simulation. All the runs shown in the figure were made with sludge S1 and a consistent loading of 2.5 lb/ft^2. In all except one run, the moisture content of the soil was 10.7 percent by weight. In the experiment with 20.7 percent soil moisture, there was a large increase in the amount of fugitive hydrocarbon loss. This effect may be due to the wetter soil being much less permeable to the liquids in the sludge. Pools of liquid were observed on the soil surface. The residence time of these liquid pools was much longer than that observed with the lower moisture soils.

In one run, the sludge was heated to 140°F before applying it to the soil surface. There was no impact of this higher temperature on the 30-minute integrated area, probably because of relatively rapid cooling. The maximum concentration and the 6-minute integrated area were somewhat higher than the base case.

The effect of soil type on the emission rate was not adequately defined in this study. When sludge S3 and soil T were used in test runs, the emissions were lower than found with soil S. This is consistent with the lower moisture content of soil T. However, emissions were higher with sludge S1 and soil T than with sludge S1 and soil S. At this point, the anomaly cannot be explained.

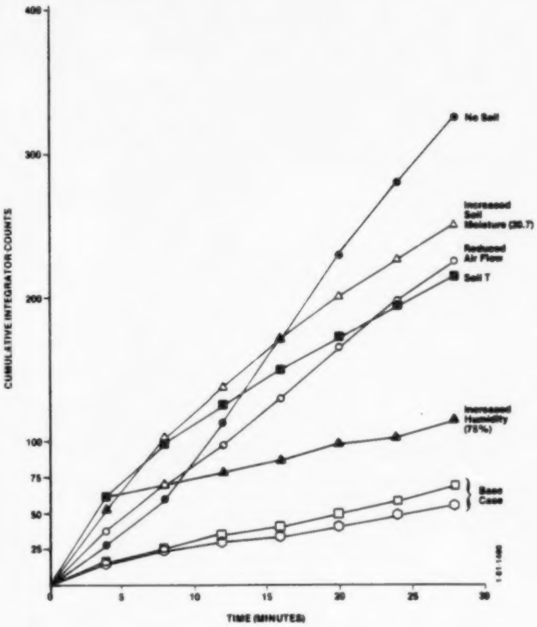


Figure 9. Effect of Moisture, Loading and Air Flow on Emissions

Figure 9 indicates that emissions increase dramatically when the air velocity is reduced from 3 mph to 1 mph. However, it should be remembered that the cumulative integrator counts are equivalent to integrated concentrations in the exiting air. Thus, a threefold increase in integrated concentration was detected for a threefold decrease in air flow rate. This is equivalent to the same mass emission for both wind speeds.

All but one experiment were run at ambient humidity (~ 50%). One run was made at approximately 75 percent relative humidity. As shown in Figure 9, there appears to be a pronounced effect on the emission rate. The cumulative emissions at 30 minutes from spreading are about twice as great at the elevated humidity level.

One test run was made with the air temperature reduced from 100°F to 80°F and the soil temperature reduced from 120°F to 100°F. The hydrocarbon emissions for the first 30 minutes following spreading were reduced by about 25 percent for the test run at lower temperatures.

Much of the variability in the data and results could not be attributed solely to the independent effects of the variables which were studied. This suggests the possibility of important interactions between these variables. Interactions were not adequately studied in this program because of constraints on the number of tests which could be made.

Conclusions

The results obtained in this study support the following conclusions:

- The laboratory landfarming simulation device developed during this study can provide very reproducible results for sludge emission studies.
- The volatility of the sludge is very important, perhaps the most important, parameter in estimating the emissions from landfarming of sludge.
- The sludge stripping test developed in this study gives a quantitative measure of the volatility of a sludge. This volatility measure appears to correlate with the landfarming emission rates.
- The emission rates are affected by the sludge loading on the soil. There may exist some low soil loading ranges which are less desirable with respect to atmospheric emissions.
- Within the range studied, air velocity does not affect the quantity of hydrocarbons emitted.
- Subsurface injection of sludges appears to be the preferred spreading technique for minimizing atmospheric emissions from landfarming operations.
- There may be important interactions between some of the variables studied in this project. These could not be investigated within the scope of this study.
- From 0.01 to 3.2 weight percent of the sludges applied to the soil in the landfarming simulations was vaporized. This is equivalent to

0.1 to 3.5 percent of the oil in the applied sample sludges.

- The highest emission rates occur within the first 30 minutes after application of the sludge.

Acknowledgments

The authors would like to thank the American Petroleum Institute and the U. S. Environmental Protection Agency for their support and guidance in this work. We would also like to acknowledge the contributions of the Radian technical staff, notably Mr. L. P. Provost, Mr. J. Randall and Dr. R. Minear who has reviewed reports and manuscripts.

THE DEVELOPMENT OF LABORATORY AND FIELD STUDIES TO DETERMINE THE FATE OF MUTAGENIC COMPOUNDS FROM LAND APPLIED HAZARDOUS WASTE

K. C. Donnelly and K. W. Brown
Texas Agricultural Experiment Station
Soil and Crop Sciences Department
Texas A&M University
College Station, Texas 77843

ABSTRACT

The future health of our citizens may well depend upon the proper disposal of the more than 40 million metric tons of hazardous waste which are produced annually. The hazards associated with improper disposal include both toxic and mutagenic responses. While toxic responses are manifested soon after exposure, mutagenic responses are much more subtle and may require decades before they are fully manifested. There are a large number of plant, microbial, and mammalian cell culture assays which have been developed to indicate the presence of compounds which cause genetic damage. In the present study, two biological systems were evaluated as part of a battery of bioassays to be used in determining the fate of mutagenic constituents from land applied hazardous waste. The Salmonella/microsome assay and Bacillus subtilis DNA repair assay were used to evaluate the genetic toxicity of a refinery and a petrochemical sludge. The two wastes were separated into acid, base, and neutral fractions by liquid-liquid extraction. All three separates exhibited mutagenic activity. The degradability of the petrochemical waste was evaluated in a laboratory study. The waste was mixed with a Norwood sandy clay and incubated in a soil respirometer for 180 days at 30°C. Following the incubation period, the residual hydrocarbons were extracted from the soil for analysis by the biological systems. The mutagenic effects of the saturate and aromatic fractions appear to be reduced by soil incubation, while no such reduction was observed in the condensed ring fraction. Additional information was collected on the mutagenicity of leachate and runoff water collected from field lysimeters amended with the two wastes. Only a few samples of the leachate contained low levels of activity, while the mutagenic activity of the runoff decreased with time following application. These results indicate that biological analysis can be useful to evaluate the fate and mobility of the mutagenic constituents of wastes disposed of by land treatment.

INTRODUCTION

A by-product of the rapid expansion of our industrial activities in recent years has been a subsequent increase in the rate of generation of hazardous waste. The EPA (1979) estimated that more than 40 million metric tons of hazardous waste would be generated in 1980. The most common methods used to dispose of this waste include landfills, deep well injection, ocean dumping, incineration, and land treatment. Of these methods, only land treatment and incineration provide for the partial or complete destruction of toxic organic waste constituents.

The use of non-destructive methods of waste disposal on the land results in dedicated sites which are removed from productivity forever. Land treatment may, however, result in sites which can be reclaimed, provided it can be demonstrated that hazardous constituents will be retained or degraded within the immediate environment of a land treatment facility. It is essential that hazardous wastes be managed so that the public is protected from the effects of waste constituents which can cause genetic damage. Genotoxic compounds in a hazardous waste must be monitored in order to control accidental exposure to mutagenic, carcinogenic, or teratogenic agents, and to prevent transmission of related defects to future generations. Genetic toxicity should be determined using a series of biological systems which will provide an accurate prediction of the potential of waste constituents to cause gene mutations and other types of genetic damage. Biological tests provide the most accurate prediction of the genetic toxicity of a sample, while chemical analysis of the components of a complex mixture may fail to account for transformations in the soil or the various interactions which can occur between chemicals in a complex mixture. There are four groups of biological test methods which may be used to evaluate the genetic toxicity of a sample. These methods include epidemiologic, long-term animal, long-term plant and animal cell culture, and simple microbial, plant or animal cell culture assays. The only one of these methods which is not restricted by time and cost is the short-term assays using plant, microbial or mammalian cell cultures. A list of some of the possible short-term systems and the genetic events which they can detect is given in Table 1.

A complete battery of test systems should be capable of detecting gene mutations, compounds which cause various types of chromosome damage, and those which inhibit DNA repair. This project used several test systems to respond to the types of genetic damage previously described, to detect the anticipated compounds of the waste, and which can incorporate metabolic activation into their testing protocol. All of these systems include provisions for solvent controls and positive controls which demonstrate the sensitivity of the test system, the functioning of the metabolic activation system, and act as an internal control for the biological system. Thus far, we have examined the use of two biological test systems to detect compounds which can cause point mutations, and those which can produce increased lethal damage in DNA repair deficient organisms. The microbial mutagenicity assay using Salmonella typhimurium as an indicator organism has been shown to be 80-95% efficient for detecting certain classes of organic chemical carcinogens (McCann et al., 1975; Purchase et al., 1976). Categories of carcinogens which are poorly detected by Salmonella assay include chlorinated hydrocarbons, chemicals which are bactericidal or volatile, and those which crosslink DNA (Rinkus and Legator, 1979). The Bacillus DNA repair assay has been shown to be sensitive to pesticides (Shiau et al., 1980) and bactericides (Brown and Donnelly, 1981) which fail to induce a clear response in Salmonella. The two biological test systems were selected to efficiently detect mutagens and potential carcinogens, with the DNA repair assay serving as a compliment to enhance the efficiency of the mutagenicity assay.

The complete battery of test systems used in this project also includes biological systems utilizing Aspergillus nidulans (Scott et al., 1980); Glycine max (Vig, 1975); and Tradescantia (Sparrow et al., 1974) as indicator organisms. The various types of chromosome damage which can be indicated by these test systems include nondisjunction, mitotic crossing over, major chromosomal damage, recessive lethals, translocation, and duplication (Scott and Kafer, 1980; Nilan and Vig, 1976).

MATERIALS AND METHODS

For the present purpose, two hazardous wastes were collected for study. These were characterized and then extracts were subjected to bioassays to detect mutagenic activity. The wastes were also incubated with soil to evaluate the fate of the mutagenic compounds when exposed to the soil environment. The same wastes were applied to the large undisturbed lysimeters from which leachate and runoff were collected. These samples were concentrated on the XAD resin. The organic residue was also evaluated for mutagenic activity.

Waste

The two wastes used in this study were collected from API oil-water separators, one from a petroleum refinery and one from a petrochemical plant. Two

TABLE 1. BIOLOGICAL SYSTEMS WHICH MAY BE USED TO DETECT GENETIC TOXICITY OF A HAZARDOUS WASTE

Organism	Genetic Event Detected		Metabolic Activation	References
	Gene Mutation	Other Types of Genetic Damage		
PROKARYOTES				
Bacillus subtilis	Forward, reverse	DNA repair	Mammalian	Felkner, Hoffman and Wells, 1979; Kada, Morija, and Tanooka, 1977; Tanooka, Munakata and Kitahara, 1978.
Escherichia coli	Forward, reverse	DNA repair	Mammalian, plant	Green, Muriel and Bridges, 1976; Mohn, Ellenberger and McGregor,1974; Slater, Anderson and Rosenkranz, 1971; Speck, Santella and Rosenkranz, 1978; Scott *et al*., 1978.
Salmonella typhimurium	Forward, reverse	DNA repair	Mammalian, plant	Ames, McCann and Yamasaki, 1975; Plewa and Gentile, 1976; Skopek *et al*., 1978.
Streptomyces coelicolor	Forward	DNA repair	Not Developed	Carere *et al*., 1975.
EUKARYOTES				
Aspergillus nidulans	Forward, reverse	DNA repair, Chromosome aberrations	Mammalian, plant	Bignami *et al*., 1974; Roper, 1971; Scott *et al*., 1978; Scott *et al*., 1980.
Neurospora crassa	Forward	Not developed	Mammalian	DeSerres and Malling, 1971; Ong, 1978; Tomlinson, 1980.
Saccharomyces cervisiae	Forward	Mitotic gene conversion	Mammalian	Brusick, 1972; Loprieno *et al*., 1974; Mortimer and Manney, 1971; Parry, 1977.
Schizosaccharomyces pombe	Forward	Mitotic gene conversion	Mammalian	Brusick, 1972; Loprieno *et al*., 1974; Mortimer and Manney, 1971; Parry, 1977.
PLANTS				
Tradescantia	Forward	Chromosome aberrations	Plant	Nauman, Sparrow and Schairer, 1976; Underbrink, Schairer and Sparrow, 1973.
Arabidopsis thaliana	Chlorophyll mutation	Chromosome aberrations	Plant	Redei, 1975.
Hordeum vulgare	Chlorophyll mutations	Chromosome aberrations	Plant	Kumar and Chauhan, 1979; Nicoloff, Gecheff and Stoilov, 1979.
Pisum sativum	Chlorophyll mutations	Chromosome aberrations	Plant	Ehrenburg, 1971.
Triticum	Morphological mutation	Chromosome aberrations	Plant	Ehrenberg, 1971.
Glycine max	Chlorophyll mutation	Chromosome aberrations	Plant	Vig, 1975.
Vicia faba	Morphological mutation	Chromosome aberrations	Plant	Kihlman, 1977.
Allium cepa	Morphological mutation	Chromosome aberrations	Plant	Marimuthu, Sparrow, and Schairer, 1970.

TABLE 1 (continued)

Organism	Genetic Event Detected Gene Mutation	Other Types of Genetic Damage	Metabolic Activation	References
INSECTS				
Drosophila melanogaster	Recessive lethals	Non-disjunction, deletions	Insect	Wurgler and Vogel, 1977.
Habrobracon	None Developed	Dominant lethals	Insect	Von Borstel and Smith, 1977.
MAMMALIAN CELLS IN CULTURE				
Chinese hamster ovaries	Forward, reverse	Chromosome aberrations	Mammalian	Neill *et al*., 1977; Beek, Klein and Obe, 1980.
V79 Chinese hamster cells	Forward, reverse	Chromosome aberrations	Mammalian	Artlett, 1977; Soderberg *et al*., 1979.
Chinese hamster lung cells	Forward	Chromosome aberrations	Mammalian	Dean and Senner, 1977.
Human fibroblasts	Forward	DNA repair	Mammalian	Jacobs and DeMars, 1977.
Human lymphoblasts	Forward	DNA repair	Mammalian	Thilly *et al*., 1976.
L5178Y mouse lymphoma cells	Forward	Chromosome abberrations	Mammalian	Clive and Spector, 1975; Clive *et al*., 1972; Clive, 1973.
P388 mouse lymphoma cells	Forward	Chromosome aberrations	Mammalian	Anderson, 1975.
Human peripheral blood lymphocytes	Forward	Chromosome aberrations	Mammalian	Evans and O'Riordan, 1975.
Various organisms	None Developed	Sister chromatid exchange	Mammalian	Perry and Evans, 1975; Stretka and Wolff, 1976.

fifty-gallon samples of each waste were collected. An aliquot of each waste was removed from the drum for use in the laboratory study, and the remainder of the waste stored until use in the field study. The physical and chemical characteristics of each waste are given in Table 2. Dichloromethane was selected from a group of agents to extract the organic fractions of the waste and the soil, since it consistently provided the greatest extraction efficiency for the wastes used. The residue from this extraction was partitioned into acid, base, and neutral fractions by liquid-liquid extraction following the scheme outlined in Figure 1.

Biodegradation

The effect of land application on the toxic potential of the petrochemical waste was evaluated in a soil respirometer (Figure 2). The waste was mixed with a Norwood sandy clay soil at two treatment rates and incubated at 30°C for 180 days at a moisture content of 18%. One set of flasks received one 5% waste application, one set received four 5% applications on days 0, 45, 90, and 135, and one which received no application of waste served as a control. Biodegradation was monitored by adsorption of evolved CO_2 onto 0.1N NaOH during the incubation period. At the end of the incubation period, 25g of the waste-soil mixture was removed and extracted with six volumes of dichloromethane prior to separation on a silica gel column. The dichloromethane extract was separated into aromatic, aliphatic and condensed ring fractions with petroleum ether, dichloromethane in petroleum ether (1:4) and dichloromethane, respectively. The effect of biodegradation on toxicity was determined by comparing mutagenicity of the soil extract towards *Salmonella typhimurium* of a fresh sample of soil-waste mixture with one that had been incubated for 180 days.

Leachate and Runoff

Leachate and runoff samples were collected from large, undisturbed field lysimeters containing four soils. Soil characteristics are given in Table 3. Each waste was incorporated into the top 15 cm of two lysimeters of each soil. A second and third waste application was made to one lysimeter of each soil, and

TABLE 2. CHARACTERISTICS OF THE SLUDGES

Oil Sludge	Extractable Carbon g C/100g	Ash	Water	CLASS % OF TOTAL HYDROCARBON Pentane	Benzene	Dichloromethane
Refinery	10	41	46	72	22	6
Petrochemical	62	25	12	63	36	1

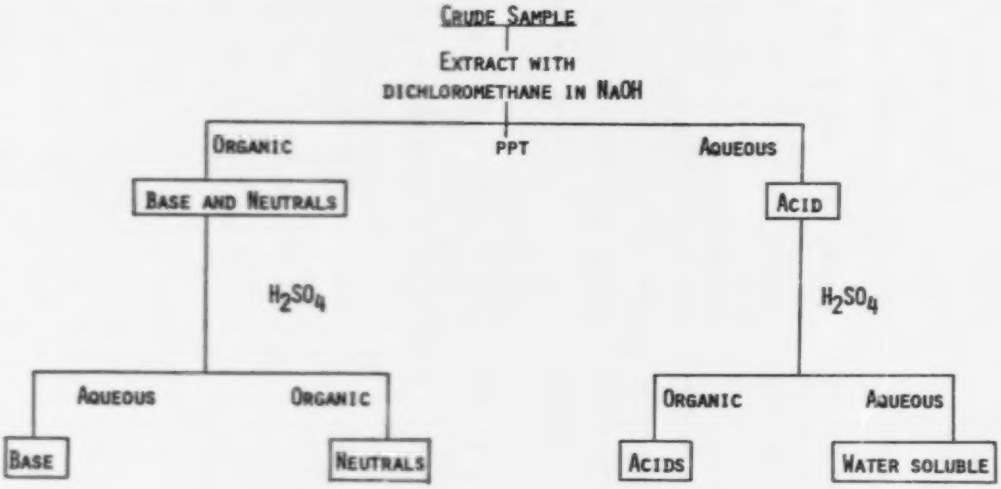


Figure 1. Schematic Diagram for Extraction Procedure Used to Separate Hazardous Waste Fractions.

one lysimeter to which no waste was applied served as a control. Five monoliths of each soil were encased in the 150 cm deep lysimeters and brought to a central location. A detailed description for the installation of lysimeters is given by Brown *et al.* (1974). The leachate was collected from porous ceramic suction cups (Coors Type # 7001-P-6-C), which were installed in the soil at the bottom of the profile. The suction cups were connected by nylon tubing to a 20 liter glass bottle which was connected to a vacuum manifold. Leachate samples were collected once a week unless the rate of water flow required a more frequent sampling schedule.

Runoff samples were collected by means of a peristaltic pump. Glass beakers were placed in a small hole in the corner of each lysimeter; the soil surface in the lysimeter was sloped so that runoff water could collect in the beaker. A rainfall of greater than 1.27 cm activated a switch which supplied power to the pumps. The collected runoff was pumped through nylon tubing to a 20 liter glass bottle where the water was stored in an air conditioned shed until collected. Water samples were collected in amber glass bottles and stored at 4°C until processed.

Two methods were employed for the extraction of water-bound organic compounds. Initially, a 20 cm^3 bed was made of non-polar XAD-2 resin (Applied Science Laboratory, State College, PA) following the methods of Hooper, *et al.*, (1978). Later in the study, it was decided, due to the complex nature of the samples being

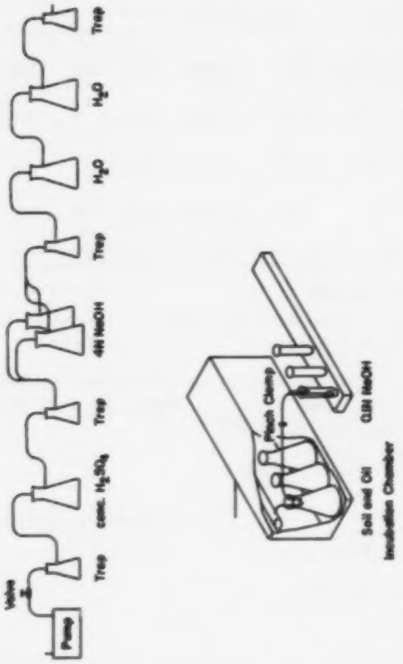


Figure 2. Schematic diagram of a respirometer.

analyzed, to supplement the XAD-2 with a moderately polar resin. Thus, samples which were extracted in the latter portion of the study were passed through a mixed bed of 4.0 g of XAD-2 and 6.3 g XAD-7 or approximately 20 cm^3 of each resin as suggested by Rappaport et al. (1979). The resins were washed prior to use by swirling and decanting three times with ten volumes each of acetone, methanol, and distilled water. Washed resins were stored at 4°C prior to use. Glass econo-columns (Bio-Rad, Richmond, CA)* 1.5 x 50 cm^2 were packed with 20 cm^3 of XAD-2 resin followed by 20 cm^3 of XAD-7 resin. A glass wool plug was placed above the resin in order to trap soil particles. The columns were flushed with 1,200 ml of distilled water before loading the water sample. Leachate or runoff water was placed in a reservoir and allowed to pass through the column by gravity flow at about 50 ml per minute. After loading the water sample, dry nitrogen was introduced into the column to remove the residual aqueous phase, and the column washed with 120 ml of distilled water to remove residual histidine. The adsorbed organic compounds were then eluted with 160 ml of acetone. The acetone extract was filtered through about 30 g of anhydrous Na_2SO_4 and Whatman No. 42 filter paper into a flat bottom flask. Extracts were reduced to less than ten milliliters on a Brinkman-Bucci Model R roto-evaporator, and taken to dryness in a screw-capped glass culture tube under a stream of nitrogen. Dimethyl sulfoxide (Sigma) was added to the dried extract at a rate of 0.5 ml DMSO/1 of unconcentrated water, and the resultant solution passed through a 0.2 µm average pore diameter Teflon filter (Millipore-Fluoropore, Bedford, Mass.). Samples were stored at 4°C prior to use.

Bioassay

The genetic toxicity of the extracted samples was measured with two microbial systems capable of detecting compounds which produce point mutations or increased lethal damage in DNA repair deficient strains. The Salmonella/microsome assay as described by Ames et al. (1975) was used to measure the ability of a sample to revert strains of bacteria to histidine prototrophy. Samples were tested in two strains at a minimum of three dose levels with and without microsome activation from Aroclor-1254 induced rat liver from Litton Bionetics (Kensington, M.D.). The procedures for the S-9 mix and the plate incorporation assay were the same as Ames et al. (1975), except that overnight cultures were grown in 5 ml of Oxoid Broth in a 125 ml Erlenmeyer flask. Positive controls as well as solvent and sterility controls were run. The control which was used to verify metabolic activation was 10 µg 2-acetylaminofluorene, while positive controls for TA 98 and TA 100 were 25 µg 2-nitrofluorine and 2 µg N-methyl-N'-Nitro-N-nitrosoguanidine, respectively. The genetic characteristics of the Salmonella and Bacillus strains used in this study are given in Table 4.

The Bacillus subtilis DNA repair assay was used to evaluate samples which

---

*Mention of brand name does not constitute endorsement.

TABLE 3. CHARACTERISTICS OF SOILS UTILIZED IN BIODEGRADATION EXPERIMENTS

Soil Series	Sand	Silt	Clay	O.M.	CEC	pH	N	P	K	Ca	Mg	% Moisture		
												WP	FC	SAT
	%				meq/100g		ppm							
Norwood	48.2	15.2	36.6	1.4	19.6	7.69	70	94	312	4,000	485	12	18	33
Nacogdoches	41.8	12.9	45.3	1.3	17.2	5.95	47	3	164	1,280	400	8	20	36
Lakeland	81.1	4.5	14.4	0.7	0.3	6.45	42	20	200	600	100	1	5	23
Bastrop	60.3	10.0	29.7	1.0	27.4	6.86	160	25	200	2,920	385	6	22	25

Table 4. Microbial Systems Used to Detect Genetic Damage

Bacteria	Strain	Genetic Event Detected	Mutation which Enhance Sensitivity*	Reference
S. typhimurium	TA 1538	frameshift mutation	hisD3052, rfa, ΔuvrB	Ames, *et al.*, 1975
	TA 98	frameshift mutation	hisD3052, rfa, ΔuvrB, pkM101	
	TA 1535	base-pair mutation	hisG46, rfa, ΔurvB	
	TA 100	base-pair mutation	hisG46, rfa, ΔurvB, pkM101	
B. subtilis	168 wt	inhibition of DNA repair	wild type	Felkner *et al.*, 1979
	rec A8	"	rec$^-$, DRC$^-$, trans$^-$	
	rec E4	"	rec$^-$	
	mc-1	"	mitomycin C sensitive	
	hcr-9	"	ΔuvrB	
	fh2006-7	"	ΔuvrB, rec$^-$	

*hisD3052, hisG46 - mutation in histidine operon
rfa-deep rough characteristic-mutants lack lippopolysacharide cell wall, enhances permeability
ΔuvrB-deficient in excision repair; sensitive to ultraviolet light
pkM101- contain R factor, plasmid which enhances sensitivity
rec$^-$ - deficient in recombinant repair
DRC$^-$ - blocked in donor-recipient complex formation
trans$^-$ - deficient in transformation and transduction

produced a toxic response in *Salmonella*. The toxicity of the samples was compared in six strains of *Bacillus subtilis* (Table 4). The procedures used were the same as in Felkner *et al.* (1979). Overnight cultures grown in Brain Heart Infusion Broth (Difco) were streaked radially from a centered sensitivity disk. and the nutrient agar plates were grown for 24 hours at 37°C. After the incubation period, the toxicity of the sample was evaluated by comparing the zone of inhibition produced. Controls included U.V. sensitivity, 2 μg mitomycin C, and 2 μl methylmethane sulfonate.

RESULTS AND DISCUSSION

Waste Characterization

Distribution of the mutagenic activity in the acid, base, and neutral fractions of the refinery and petrochemical waste is given in Table 5. Additional information is presented on the activity of crude oil (Epler *et al.*, 1978) and cigarette smoke condensate (Kier *et al.*, 1976) for comparison purposes. Cumulative mutagenic activity of both the refinery and the petrochemical waste appear to be greater than for unrefined crude oil

TABLE 5. DISTRIBUTION OF MUTAGENIC ACTIVITY IN FRACTIONS OF SEVERAL COMPLEX MIXTURES

Sample	Revertants/mg			Reference
	Acid	Base	Neutral	
Refinery Waste	813	2,308	33	
Petrochemical Waste	498	278	246	
Crude Oil	10	277	150	Epler *et al.*, 1978
Cigarette Smoke	5,450	430	1,940	Kier *et al.*, 1976

(437 revertants/mg), but considerably less than for cigarette smoke condensate (7,820 revertant/mg). For the two wastes studied, the basic fraction of the refinery waste induced the greatest response, generating more than 2,000 revertants/mg of residue. The mutagenic activity of the petrochemical waste was distributed more evenly among the acid, base and neutral fractions, with the greatest activity detected in the acid fraction (498 revertants/mg).

Biodegradation

The mutagenic activity in unamended soil, soil with 5% waste which had not been incubated, soil with 5% waste and soil with 20% waste both which had been incubated for 180 days at 30°C are given in Table 6. No activity was evident in any of the fractions from the unamended soils. At the highest application rate, the number of revertants induced by the saturate and aromatic fractions was reduced by 21 and 26% respectively. The toxic potential of the saturate and aromatic fractions was reduced to a greater extent at the lowest application rate, although the dichloromethane fraction representing condensed ring compounds failed to exhibit a similar reduction at either application rate. Other researchers (Dibble and Bartha, 1979) have reported an increase in the concentration of residual condensed ring fractions after soil incubation. This increase may be due to the accumulation of metabolites from other fractions, and could explain the increase in observed mutagenic activity in this fraction. With adequate time, the condensed ring fractions should also degrade, reducing the activity of the residual materials.

When the mutagenic activity of incubated and non-incubated soil is expressed as revertants per gram of soil, the reduction produced by chemical and biological activity becomes more evident. The results in Table 7 show a significant reduction in the mutagenic activity of both the saturate and aromatic fractions. As discussed earlier, the dichloromethane extract did not show a reduction in mutagenic activity after six months of incubation.

The extraction efficiency of these procedures for hydrocarbons and mutagenic activity from soil are given in Table 8. These results indicate that less than 5% of the applied hydrocarbons remained in the soil after solvent extraction. The efficiency of the recovery of mutagenic activity from soil was significantly less than for the hydrocarbons. The dichloromethane extract of the soil-waste mixture recovered only 67% of the mutagenic activity extracted from the waste alone with dichloromethane. It is unknown at this time whether the reduction was a result of soil binding, or an artifact created by the solvent extraction. Work conducted in the future will attempt to better define the cause of this deficiency so that the extraction efficiency can be improved.

Leachate and Runoff Water Samples

The mutation frequency of the leachate and runoff water collected from field lysimeters was calculated using the method of Commoner (1976) in which a mutation frequency greater than one indicates a doubling of revertant colonies. The

TABLE 6. EFFECT OF SOIL INCUBATION ON MUTAGENIC ACTIVITY OF PETROCHEMICAL WASTE

Sample	Revertant/mg Solvent Extract		
	Petroleum Ether Extract	Petroleum Ether: Dichloromethane	Dichloromethane
Soil	0	0	0
5% Waste and Soil (Not incubated)	33	479	100
5% Waste and Soil (Incubated)	24	107	112
20% Waste and Soil (Incubated)	26	354	111

TABLE 7. MUTAGENIC ACTIVITY EXTRACTED FROM SOIL AND WASTE AMENDED SOIL

Sample	Revertant/g soil		
	Petroleum Ether Extract	Petroleum Ether: Dichloromethane	Dichloromethane
Soil	0	0	0
5% Waste and Soil (Not incubated)	1.3	1.9	3.8
5% Waste and Soil (Incubated)	0.3	1.8	3.9

TABLE 8. EFFICIENCY OF EXTRACTION OF HYDROCARBONS AND MUTAGENIC ACTIVITY FROM SOIL EXTRACTION EFFICIENCY (%)

Sample	Petroleum Ether Extract	Petroleum Ether: Dichloromethane	Dichloromethane
Hydrocarbon	99	98	95
Mutagenic Activity	85	95	67

mutation frequency was calculated as:

$$MF = \frac{E-C}{C_{Ave.}}$$

where E = number of revertant colonies on an experimental plate with the residue from 200 ml of water

C = number of revertant colonies on the solvent control plates from the same day with the same tissue preparation

$C_{Ave.}$ = overall average of revertant colonies for solvent control plates for the whole period of study.

Using this scheme, a sample which

induces a mutation frequency between 1 and 1.5 is considered to have a borderline mutagenic potential, while a compound which induces a mutation frequency greater than 1.5 is considered to be a positive mutagen.

The analysis of water collected from the refinery waste-amended soil (Table 9) indicates that the leachate water samples with the greatest mutagenic activity were collected within two months after the first waste application. This data represents a summary of the mutation frequencies calculated from dose response curves where the leachate or runoff water was tested at a minimum of three dose levels. The first leachate water collected from the Bastrop clay on the 47th day after application and from the Norwood soil on the 17th day after application, induced mutation frequencies of 6.7 and 5.1 respectively. All but one of the subsequent leachate samples collected induced a mutation frequency equal to or less than 1.5. None of the water samples collected from unamended soils induced a significant increase in the number of revertants at the dose levels of water concentrate tested.

While the runoff water samples collected from the Bastrop lysimeters did exhibit a reduction in toxic potential with time, the potential remained significantly above background levels. Runoff samples collected from the Bastrop soil 40 and 145 days following the second waste application induced mutation frequencies of 9.0 and 4.2 respectively.

After the second waste application on Lakeland sand, eight runoff samples were collected over a period of 138 days. Five of the first six samples produced a clear positive response in the mutagenicity assay. The dose-response curves for these samples, presented in Figure 3, indicate that samples collected 131 and 138 days after waste application failed to induce a doubling of revertant colonies. Thus, the toxic potential of runoff water from refinery waste-amended Lakeland sand appears to have returned to background levels within five months after the second waste application. The dose-response curves for runoff water collected from unamended soil (Figure 4) indicate that even at higher water concentrate dose levels, there was no mutagenic response.

Analysis of the leachate and runoff water collected from petrochemical waste-amended soils are presented in Table 10. Only three of the leachate samples collected induced a positive response in the mutagenicity assay. Two of these were collected from the Norwood soil 38 and 52 days after the first and third waste application,respectively. One sample collected more than six months after the second waste application from the Nacogdoches soils induced a mutation frequency of 3.3. None of the leachate samples collected from the Bastrop soil induced a mutation frequency greater than 1.5.

The analysis of runoff water from petrochemical waste-amended soil indicates that large quantities of mutagenic compounds are being released at the soil surface. Runoff water collected from the Bastrop soil 38 days after the first waste application, and 113 days after the second waste application induced mutation frequencies of 14.3 and 8.4 respectively. One runoff sample from the Norwood soil and two from the Lakeland sand, all of which were collected during the winter, had mutation frequencies greater than 1.5.

The results of the analysis of leachate and runoff water by the *Bacillus subtilis* DNA repair assay are given in Tables 11 and 12. These results indicate that there is a negative correlation between mutagenicity in *Salmonella* and toxicity to *Bacillus subtilis*. None of the runoff samples which were mutagenic were also toxic in the DNA repair assay, while most of the samples which were toxic to *S. typhimurium* at higher dose levels produced increased lethal damage in repair deficient strains of *B. subtilis*. A runoff sample from petrochemical waste amended soil collected 130 days after the second waste application from the Lakeland sand produced a clear positive response in the DNA repair assay and was not mutagenic in the *Salmonella* assay. Thus, it is evident from these results that the DNA repair assay serves as a compliment to the mutagenicity assay by responding to mutagenic compounds not detected by a *Salmonella* assay and by detecting a second type of genetic damage.

TABLE 9. MUTATION FREQUENCY OF RUNOFF AND LEACHATE WATER COLLECTED FROM REFINERY WASTE AMENDED SOILS. WASTE WAS APPLIED ON DAY 0, 202 and 403. THE SYMBOL (-) MEANS NO SAMPLES WAS AVAILABLE

	TIME (DAYS)																						
	0	17	47	67	155	228	250	260	275	293	318	322	330	335	345	355	375	388	395	410	420	465	475
LEACHATE																							
Bastrop	-	-	6.7	0.9	0.2	0.4	-	0.3	-	0.2	-	-	-	-	-	0.6	-	1.6	-	0.1	1.1	-	-
Norwood	-	5.1	0.7	-	-	-	-	-	-	-	-	-	0.1	-	-	-	0.7	-	-	-	1.5	-	0.1
Nacogdoches	-	-	-	-	-	-	-	0.5	-	0.3	-	-	0.3	-	-	-	0.1	-	-	1.5	0.2	0.1	1.4
RUNOFF																							
Bastrop	-	-	-	1.4	-	-	9.0	-	-	-	-	-	-	0.3	0.4	4.2	-	-	2.6	2.7	-	-	-
Lakeland	-	-	-	-	-	-	-	1.6	0.8	1.9	5.3	1.8	2.5	0.3	0.3	-	-	-	-	-	-	-	-
LEACHATE																							
Unamended soil	-	-	0.5	0	0.1	-	-	0.1	-	0.8	0.1	-	-	-	-	-	-	-	-	0.12	0.8	-	-
RUNOFF																							
Unamended soil	-	-	-	-	-	0	0.3	-	0.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-

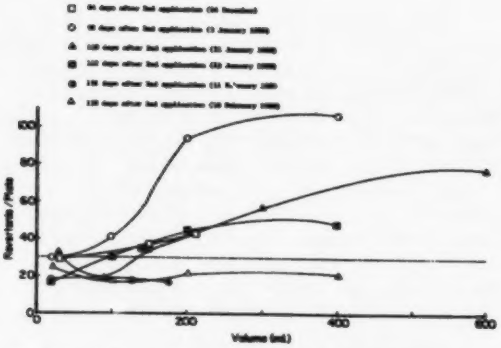


Figure 3. Mutagenicity, as measured with S. typhimurium strain TA98 without enzyme activation of runoff water from refinery waste amended Lakeland sand.

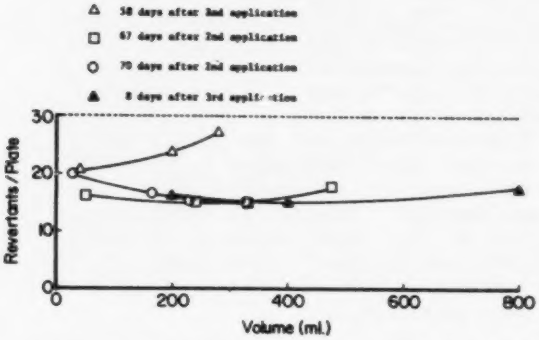


Figure 4. Mutagenicity, as measured with S. typhimurium TA 98, of runoff water from unamended soils. Line of significance (---) is equal to two times the number of spontaneous revertants.

CONCLUSIONS

The results obtained from preliminary testing with two petroleum sludges indicate that short-term bioassays can be a valuable tool for evaluating the mutagenic activity of a hazardous waste. The analysis of the refinery and petrochemical waste indicates that they are more mutagenic than crude oil and that they possess less mutagenic activity on a per weight basis than cigarette smoke condensate.

These procedures also seem adaptable for the determination of the treatment potential of a hazardous waste. Although it has been determined that mutagenic materials can be extracted from soil,these methods will require further development to determine the extraction efficiency of various solvents. The determination of the extent of reduction of the hazardous characteristics of a land applied waste is an essential element to the success of the land treatment method of waste disposal. Incubation studies revealed that the mutagenic activity of the waste added to soils decreased over a six month period.

Bioassays have also been shown to be effective for evaluating the level of

TABLE 10. MUTATION FREQUENCY OF LEACHATE AND RUNOFF WATER COLLECTED FROM PETROCHEMICAL WASTE AMENDED SOILS WASTE WAS APPLIED ON DAY 0, 202 AND 403. THE SYMBOL (-) MEANS NO SAMPLE WAS AVAILABLE

	TIME(DAYS)														
	0	38	53	60	70	148	153	183	190	202	245	255	263	268	280
LEACHATE															
Bastrop	-	0.3	1.4	-	0.7	1.2	0	0.3	-	-	-	-	-	-	-
Nacogdoches	-	-	-	-	-	-	-	-	-	-	-	-	1.2	1.3	-
Norwood	-	5.8	-	-	1.1	-	-	-	-	-	-	-	-	-	-
RUNOFF															
Bastrop	-	14.3	-	0.5	-	-	-	-	-	-	-	1.1	-	-	-
Norwood	-	-	-	-	-	-	-	-	-	-	1.0	-	-	-	1.3
Lakeland	-	-	-	1.1	-	-	-	-	1.5	-	-	-	-	-	0.7

TABLE 10 (CONTINUED).

	TIME (DAYS)													
	295	305	315	325	332	340	345	383	410	420	430	455	468	495
LEACHATE														
Bastrop	-	-	-	-	-	-	-	-	-	0.5	-	-	-	-
Nacogdoches	-	0.8	-	-	-	-	-	3.3	-	0.9	1.0	0.7	-	-
Norwood	-	-	-	-	-	-	-	-	0.6	-	0.1	3.1	1.5	0.5
RUNOFF														
Bastrop	-	-	8.4	-	-	-	-	-	-	-	0.6	-	-	-
Nacogdoches	0.7	-	1.5	0.7	1.6	-	0.9	-	-	-	-	-	-	-
Norwood	1.8	-	4.2	2.8	0.6	0.7	0.9	-	-	-	-	-	-	-
LEACHATE														
Unamended soil	0.8	-	-	0.1	-	-	-	-	0.2	0.8	-	-	-	-
RUNOFF														
Unamended soil	-	-	-	-	-	-	-	-	-	-	-	-	-	-

mutagenic activity in the effluent from a land treatment facility. Only low levels of mutagenic activity were detected in a few samples of leachate water collected shortly after waste application. This indicates that the soil retained the majority of the mutagenic constituents and prevented them from entering the groundwater. The runoff water collected during the year after waste application exhibited decreasing amounts of activity. The most active sample of runoff water was 14.3 times the background level. At this level, 3 liters of water could contain the activity of one cigarette.

As these systems are further developed, and the testing protocol better defined, short-term bioassays will increase in their utility for the detection and characterization of mutagens and potential carcinogens. Test systems which are used as part of a monitoring system should be selected with regards to the types of compounds in the waste, and the types of damage caused by these compounds. Additional work to be performed as part of this project will include the complete characterization of three additional hazardous wastes, along with a comprehensive greenhouse and lysimeter study to determine the treatment potential and the environmental fate of hazardous waste constituents. Although additional work is needed to more clearly define the advantages and limitations of short-term testing, the preliminary results indicate that short-term tests can be a valuable tool for use in defining the mutagenic characteristics of a waste, for evaluating their treatment potential, and for evaluating their fate and mobility from land treatment disposal sites.

TABLE 11. COMPARISON OF LETHAL EFFECT OF WATER EXTRACTS ON DNA REPAIR DEFICIENT AND PROFICIENT STRAINS OF *B. subtilis*

SAMPLE			INHIBITION RADIUS (mm)						
			168 wt	recA8	mc-1	recE4	hcr-9	fh2006-7	Response
RUNOFF REFINERY									
Soil	Volume	Day							
Bastrop	400 ml eq	335	3	-	-	-	-	3	-
Bastrop	400 ml eq	345	7	9	9	7	9	8	-
Bastrop	400 ml eq	355	6	5	6	-	6	4	-
Lakeland	400 ml eq	275	0	0	0	0	0	0	-
Lakeland	400 ml eq	293	8	5	4	3	8	6	-
Lakeland	400 ml eq	318	3	5	5	3	4	4	-
RUNOFF CONTROL									
Lakeland	400 ml eq	315	4	3	4	4	4	4	-
POSITIVE CONTROL									
Methylmethane sulfonate	2 µl	-	8	33	26	21	17	20	+++

TABLE 12. COMPARISON OF LETHAL EFFECT OF WATER EXTRACTS ON DNA REPAIR DEFICIENT AND PROFICIENT STRAINS OF *B. subtilis*

SAMPLE			INHIBITION RADIUS (mm)						
			168 wt	recA8	mc-1	recE4	hcr-9	fh2006-7	Response
RUNOFF PETROCHEMICAL									
Soil	Volume	Day							
Bastrop	400 ml eq	255	6	10	9	-	7	9	+
Bastrop	400 ml eq	315	8	7	10	-	9	5	±
Bastrop	400 ml eq	430	9	5	5	8	9	10	-
Lakeland	400 ml eq	280	2	3	2	5	4	4	±
Lakeland	400 ml eq	295	5	6	4	-	5	5	-
Lakeland	400 ml eq	315	4	4	3	4	4	4	-
Lakeland	400 ml eq	325	5	6	5	5	5	7	-
Lakeland	400 ml eq	332	3	4	4	5	8	10	+ +
Lakeland	400 ml eq	340	1	1	1	-	1	1	-
Norwood	400 ml eq	280	2	5	5	5	3	3	±
Norwood	400 ml eq	295	4	5	4	5	5	4	-
Norwood	400 ml eq	315	4	7	5	5	4	4	±
Norwood	400 ml eq	325	4	4	3	8	5	6	±
Norwood	400 ml eq	332	7	7	6	8	6	9	-
Norwood	400 ml eq	345	5	3	4	5	8	10	+ +
Norwood	400 ml eq	352	4	3	2	-	4	3	-

REFERENCES

1. Ames, B. N., J. McCann, and E. Yamasaki. 1975. Methods for detecting carcinogens and mutagens with the Salmonella/mammalian microsome mutagenicity test. Mutat. Res. 31:347.

2. Anderson, D. 1975. The selection and induction of 5-iodo-2 deoxyuridine and thymidine variants of P 388 mouse lymphoma cells with agents which are used for selection. Mutat. Res. 33: 399.

3. Arlett, C. F. 1977. Mutagenicity testing with V79 Chinese hamster cells. *In* B. J. Kilbey, M. Legator, W.Nichols and C. Ramel (ed.) Handbook of mutagenicity test procedures. p. 175-191. Elsevier Biomedical Press, Amsterdam.

4. Beek, B., G. Klein, and G. Obe. 1980. The fate of chromosomal aberrations in a proliferating cell system. Biol. Zentralbl. 99(1):73-84.

5. Bigani, M., G. Morpurgo, R. Pagliani, A. Carare, G. Conte, and G. DiGuideppe. 1974. Non-disjunction and crossing over induced by pharmaceutical drugs in *Aspergillis nidulans*. Mutat. Res. 26: 159.

6. Brown, K. W., C. J. Gerard, B. W. Hipp and J. T. Ritchie. 1974. A procedure for placing large undisturbed monoliths in lysimeters. Soil Sci. Soc. of Amer. 38: 981-983.

7. Brown, K. W., and K. C. Donnelly. 1981. Genetic toxicity of water concentrates from the effluent of a waste oil storage pond. (In Review).

8. Brusick, D. J. 1972. Induction of cyclohexamide resistant mutants in Saccharomyces cerevisiae with N-methyl-N-nitro-N-nitrosoguanine and ICR-170. J. Bacteriol. 109: 1134.

9. Carere, A., G. Morpurgo, G. Cardamone, M. Bignami, F. Aulicino, G. DiGuisepie, and C. Conti. 1975. Point mutations induced by pharamaceutical drugs. Mutat. Res. 29: 235.

10. Clive, D. W., W. G. Flamm, M. R. Machesko, and N. H. Bernheim. 1972. Mutational assay system using the thymidine kinase locus in mouse lymphoma cells. Mutat. Res. 16:77.

11. Clive, D. W. and J.F.S. Spector. 1975. Laboratory procedure for assessing specific locus mutations at the TK locus in cultured L5178Y mouse lymphoma cells. Mutat. Res. 31: 17.

12. Dean, B. J. and K. R. Senner. 1977. Detection of chemically induced mutation in Chinese hamsters. Mutat. Res. 46: 403.

13. Deserres, F. J. and H. V. Malling. 1971. Measurement of recessive lethal damage over the entire genome and at two specific loci in the ad-3 region of a two component heterokaryon of Neurosporo crassa. 2:311-341. *In* A Hollaender (ed.). Chemical mutagens, principles and methods for their detection. Plenum Press. New York.

14. Ehrenburg, L. 1971. Higher plants. 2: 365-386. *In* A. Hollaender (ed.). Chemical mutagens, principles and methods for their detection. Phenum Press, New York.

15. EPA. 1979. Subtitle C. Resource and conservation recovery act of 1976; Draft environmental impact statement. Office of Solid Waste, EPA, Washington, D.C.

16. Epler, J. L., Jennifer A. Young, A. A. Hardigree, T. K. Rao, M. R. Guerin, I. B. Rubin, C. H. Ho, and B. R. Clark. 1978. Analytical and biological analyses of test materials from the synthetic fuel technologies. Mutat. Res. 57: 265-276.

17. Felkner, I.C., K. M. Hoffman, and B.C. Wells. 1979. DNA - damaging and mutagenic effect of 1,2- Dimethylhydrazine on bacillus subtilis repair-deficient mutants. Mutat. Res. 28: 31-40.

18. Green, M. H. L., W. J. Muriel, and B. A. Bridges. 1976. Use of a simplified fluctuation test to detect low levels of mutagens. Mutat. Res. 38:33.

19. Hooper, K., C. Gold, and B. N. Ames. 1978. Development of methods for mutagenicity testing of wastewater and drinking water samples. Report to Water Resources Control Board, State of California, Sacramento, California.

20. Kada, T., M. Morija, and Y. Shirasu. 1974. Screening of pesticides for DNA interactions by REC-assay and mutagenic testing and frameshift mutagens detected. Mutat. Res.26:243.

21. Kier, L. D., E. Yamasaki, and B.N. Ames. 1974. Detection of mutagenic activity in cigarette smoke condensates. Proc. Nat. Acad. Sci. USA, 71 (10) 4159-4163.

22. Kihlman, B. A. 1977. Root tips of Vicia fava for the study of the induction of chromosomal aberrations. p. 389-410. *In* B. J. Kilbey, M. Legator, W. Nichols, and C. Ramel (ed.). Handbook of mutagenicity test procedures. Elsevier Biomedical Press, Amsterdam.

23. Loprieno, N., R. Barale, C. Bauer, S. Baroncelli, G. Bronzetti, A. Cammellini, A. Cinci, G. Corsi, C. Leporini, R. Nieri, M. Mozzolini, and C. Serra. 1974. The use of different test systems with yeasts for the evaluation of chemically induced gene conversions and gene mutations. Mutat. Res. 25: 197.

24. Marimuthu, K. M., A. H. Sparrow, and L. A. Schairer. 1970. The cytological effects of space flight factors, vibration, clinostate, and radiation on root tip cells of *Tradescantia* and *Allium cepa*. Radiation Res. 42: 105.

25. Mohn, G., J. Eltenberger, and D. B. McGregor. 1974. Development of mutagenicity tests using Escherichia coli K-12 as an indicator organism. Mutat. Res. 23:187.

26. Mortimer, R. K. and T. R. Manney. 1971. Mutation induction in yeast. 1:289-310. *In* A. Hollaender (ed.). Chemical mutagens, principles and methods for their detection. Plenum Press, New York.

27. Nauman, C. H., A. H. Sparrow, and L. A. Schairer. 1976. Comparative effects of ionizing radiation and two gaseous chemical mutagens on somatic mutation induction in one mutable and two non-mutable clones of *Tradescantia*. Mutat. Res. 38: 53-70.

28. Neill, J. P., P. A. Brimer, R. Machanoff, G. P. Hirseh, and A. W. Hsie. 1977. A quantitative assay of mutation induction at the HGPRT locus in Chinese hamster ovary cells: development and definition of the system. Mutat. Res. 45:91.

29. Nilan, R. A. and B. K. Vig. 1976. Plant test systems for detection of chemical mutagens. p. 143-170. *In* A. Hollaender (ed.). Chemical Mutagens. Vol. 4. Plenum Publishing Co., New York.

30. Ong, T. N. 1978. Use of the spot, plate and suspension test systems for the detection of the mutagenicity of environmental agents and chemical carcinogens in Neurospora crassa. Mutat. Res. 54:121-129.

31. Parry, J. M. 1977. The use of yeast cultures for the detection of environmental mutagens using a fluctuation test. Mutat. Res. 46: 165.

32. Perry, P. and H. J. Evans. 1975. Cytological detection of mutagen-carcinogen exposure by sister chromatid exchange. Nature (London). 258: 121.

33. Plewa, M. J. and J. M. Gentile. 1976. The mutagenicity of atrazine: a maize-microbe bioassay. Mutat. Res. 38:287-292.

34. Rappaport, S.M., M. G. Richard, M.C. Hollstein, and R. E. Talcott. 1979. Mutagenic activity in organic wastewater concentrates. Envir. Sci. and Technol. 13(8) 957-961.

35. Redei, G. P. 1975. Arabadopsis as a genetic tool. Ann. Rev. Genet. 9: 111-125.

36. Rinkus, S. J., and M. S. Legator. 1979. Chemical characterization of 465 known or suspected carcinogens and their mutagenic activity in the *Salmonella typhimurium* system. Cancer Research. Volume 39: 9. p. 3289-3804.

37. Roper, J. A. 1971. *Aspergillus*. *In* A. Hollaender (ed.). Chemical mutagens, principles and methods for their detection. Plenum Press, New York.

38. Scott, B. R., A. H. Sparrow, S. S. Lamm, and L. Schairer. 1978. Plant

metabolic activation of EDB to a mutagen of greater potency. Mutat. Res. 49: 203-212.

39. Scott, B. R., E. Kafer, G. L. Dorn, and R. Stafford. 1980. *Asperigillus nidulans*: systems and results of test for induction of mutation and mitotic segregation. Mutat. Res. (In press).

40. Shiau, S.Y., R. A. Huff, B. C. Wells, and I.C. Felkner. 1980. Mutagenicity and DNA-Damaging activity for several pesticides tested with *Bacillus* mutants. Mut. Res. 71: 169-179.

41. Skopek, T. R., J. L. Liber, J. J. Krowleski, and W. G. Thilly. 1978. Quantitative forward mutation assay in *Salmonella typhimurium* using 8-azaguanine resistance as a genetic marker. Proc. Nat'l. Acad. Sci. 75:410.

42. Slater, E., M. D. Anderson, and H. S. Rosenkranz. 1971. Rapid detection of mutagens and carcinogens. Cancer Res. 31: 970.

43. Soderberg, K., J. T. Mascarello, G. Breen, and I. E. Scheffler. 1979. Respiration deficient Chinese hamster cell mutants genetic characterization. Somatic Cell Genet. 5(2) 225-240.

44. Sparrow, A. H., L. A. Schairer and R. Villalobos-Pietrini. 1974. Comparison of somatic mutation rates induced in *Tradescantia* by chemical and physical mutagens. Mutation Res. 26 : 265-276.

45. Speck, W. T., R. M. Santella, and H. S. Rosenkranz. 1978. An evaluation of the prophage induction (inductest) for the detection of potential carcinogens. Mutat. Res. 54: 101.

46. Stetka, D. G. and S. Wolff. 1976. Sister chromatid exchange as an assay for genetic damage induced by mutagen-carcinogens. Mutat. Res. 41: 333.

47. Tanooka, H., N. Munakata, S.Kitahara. 1978. Mutation induction with UV- and X-radiation in spores and vegetative cells of *Bacillus subtilis*. Mutat. Res. 49: 179-186.

48. Thilly, W. G., J. G. DeLuca, I.V.H. Hoppe, and B. W. Penmann. 1976. Mutation of human lymphoblasts by methylnitrosourea. Chem. Biol. Interact. 15:33.

49. Tomlinson, C.R. 1980. Effects of pH on the mutagenicity of sodium azide in *neurospora-crassa* and *Salmonella-typhimurium*. Mutat. Res. 70(2): 179-192.

50. Underbrink, A.G., L. A. Schairer, and A. H. Sparrow. 1973. *Tradescantia* stamen hairs. A radiobiological test system applicable to chemical mutagenesis. 3: 171-207. *In* A. Hollaender (ed.). Chemical mutagens, principles and methods for their detection. Plenum Press, New York.

51. Vig, B. K. 1975. Soybean (*Glycine max*): a new test system for study of genetic parameters as affected by environmental mutagens. Mutat. Res. 31: 49-56.

52. Von Borstel, R. C. and R. H. Smith. 1977. Measuring dominant lethality in Habrobracon. p. 375-387. *In* B. J. Kilbey, M. Legator, W. Nichols and C. Ramel (ed.). Handbook of mutagenicity testing procedures. Elsevier Biomed. Press, Amsterdam.

53. Wurgler, F. E. and E. Vogel. 1977. Drosophila as an assay system for detecting genetic changes. p. 335-373. *In* B. J. Kilbey, M. Legator, W. Nichols, and C. Ramel (ed.). Handbook of mutagenicity test procedures. Elsevier Biomed. Press, Amsterdam.

CLOSURE TECHNIQUES AT A PETROLEUM LAND TREATMENT SITE

John E. Matthews
Fred M. Pfeffer
Lawrence A. Weiner
U.S. Environmental Protection Agency

ABSTRACT

Land treatment is noted in the hazardous waste regulations as one of the technologies for the treatment and disposal of hazardous wastes. Interim status regulations on land treatment were published in the Federal Register, May 19, 1980 (Vol. 45 FR 33153). These regulations require that the owner or operator of a hazardous waste land treatment facility develop a closure plan that will control the release of contaminants from the site.

Two objectives of the EPA land treatment research program are: (1) determine the extent of migration of pollutants through the soil at closed land treatment facilities, and (2) compare the efficacy of different closure techniques. Two projects that have recently been funded will attempt to satisfy these objectives.

The first project will be conducted by the University of Oklahoma. Three closed oily waste land treatment sites will be selected to provide information on the extent of contaminant migration in the soil. The second study, a cooperative agreement between EPA and the American Petroleum Institute, will compare the efficacy of four closure techniques over a three-year period--(1) revegetating the site, (2) closing the site like a landfill, (3) removing the soil, and (4) leaving the site as is.

INTRODUCTION

Land treatment is one of the land disposal technologies for the management of hazardous wastes. The practice involves the application of waste to the soil followed, in most cases, by incorporation of the waste into the soil by conventional farm equipment (e.g., disc, rototiller). The purpose of land treatment is the degradation and attenuation of wastes by biological, chemical, and physical reactions occurring in or on the soil. The Agency considers land treatment to be especially effective for hazardous wastes that are high in degradable organics and relatively low in heavy metals.

Since the general objective of land treatment is the microbial degradation of organic waste constituents, this waste management practice has been used primarily to treat oily waste. The petroleum industry has been utilizing the land treatment concept for residual disposal for at least 25 years [Berkowitz, (1) Huddleston (3)]. Several existing petroleum refineries use some modification of this treatment method [CONCAWE (2)]. Examples of the application of land treatment by U.S. refineries are given in Table 1.

Interim status regulations on land treatment of hazardous wastes were published by EPA in the Federal Register, May 19, 1980, (45 FR 33153). The standards address all aspects of land treatment including: control of surface water run-on and contaminated run-off, waste analysis, monitoring, and closure/post-closure care. The standards for closure are couched in a framework that permits the manager or operator of a particular site to develop and implement a closure plan that best suits the site. The standards provide direction in the form of general human health and environmental objectives which must be addressed by the closure plan. In addition, certain factors

TABLE 1. EXAMPLES OF THE APPLICATION OF LAND TREATMENT BY U.S. REFINERIES

Refinery	Type of Sludge	Farming Technique	Application Rate	Treatment Experiences	Soil Type	Land Area
1	Separator sludge	Spread by bulldozer; Disc into soil after drying for 1 month.	10-12 cm depth of sludge	More than 20 years	Clay	75-100 acres
2	Separator sludge; tank bottoms; stable emulsions.	4 sections worked in rotation & mixed with bulldozer 2-4 times per month.	15 cm of sludge mixed with 15 cm of soil.	Since 1961	Clay	7 acres
3	Oily sludge from lagoons.	Single application of 10-yr. accumulation from lagoons; mixed by discing.	10-12 cm of sludge mixed with soil to depth of 45 cm.	Since 1969	Silty loam surface; clay subsoil.	...
4	Desalter & tank cleanings, separator bottoms; spill cleanings; biosludge; filter clays.	Land-spreading on quadrants during 9 months of year; mixed by discing once a week.	8-15 cm depth of sludge mixed with soil to depth of 15-20 cm.	Experimental scale 1972. Full scale since mid 1973.	...	8 acres
5	Separator sludge; biosludge.	Spreading followed by disc-harrowing when partially dried.	8-10 cm depth of sludge.	...	...	...

are identified which must be considered in the closure plan when addressing the above objectives.

The use of performance standards for closure was preferred because the dearth of information on closing land treatment facilities precluded setting design and operating standards. Since the land treatment process is relatively new, virtually no experience with closure has been gained. The projects described below are expected to provide information on the fate of contaminants in closed land treatment facilities and the efficacy of potential closure techniques.

CLOSURE OPERATIONS

The objective of a closure operation is to prevent the occurrence of any future environmental or health hazards as mandated by RCRA.

Under the interim status regulations, the owner or operator of a land treatment facility must develop and implement a facility closure plan, the terms of which are enforceable against him. The plan must address four objectives:

(1) controlling migration of hazardous waste and hazardous waste constituents into groundwater.

(2) controlling release of contaminated runoff to surface water.

(3) controlling release of airborne particulate contaminants.

(4) compliance with standards established for food crops.

The owner or operator must consider a range of factors affecting the ability of the facilities to meet these objectives. These factors include: the waste, the climate, the site location, the soil, and the depth of contaminant migration. He must also consider the applicability of various closure methods, including removal of the soil, runoff collection and treatment, use of cover materials, diversion structures, and additional monitoring.

Two objectives of the EPA land treatment research program are: (1) determine the extent of migration of pollutants through the soil at closed land treatment facilities, and (2) compare the efficacy of different closure techniques. In order to satisfy these objectives and support the regulatory efforts of the Office of Solid Waste, EPA has recently funded two projects to satisfy these objectives. Following is a discussion of the proposed experimental designs for these two projects.

EVALUATION OF CLOSURE TECHNIQUES AT OILY WASTE LAND TREATMENT FACILITIES

The objective of this study is to obtain information, over a 3-year period, on the efficacy of four potential closure techniques for oily waste land treatment facilities. The project is being performed under a cooperative agreement between the American Petroleum Institute (API) and EPA.

The four closure techniques to be investigated include: (1) establish a vegetative cover on the site, (2) close the site as a landfill, (3) remove the contaminated soil, and (4) leave the site as is.

Establishing a vegetative cover may be the most economical method if it will prevent erosion of the soil that was used as a treatment medium. The effects a vegetative cover will have on runoff quality, waste migration, and degradation on any remaining waste residuals will be investigated. Because of the inhibitory effect a vegetative cover has on waste degradation, it may be advantageous to postpone covering the site until most of the waste residuals have degraded.

Closing the site as a landfill will require the placement of a natural or synthetic cap over the contaminated soil. Although capping a land treatment facility may retard infiltration of rainwater and prevent erosion, it will also alter or even curtail the biological degradation of remaining waste residuals. In addition, the previously aerobic zone of incorporation will become anaerobic. Under anaerobic conditions biological degradation is slow and incomplete. The oxidation state of any metals bound to the soil will change, and the pH of the soil will slowly drop as organic acids are produced. These phenomena and the effects they will have on contaminant migration will be investigated.

Removing the soil from a closed land treatment facility requires only engineering and economic calculations. The costs for soil removal and the landfilling of the soil can be estimated from existing construction practices. After the soil is removed, new soil will be brought in, and the site will be regraded and a vegetative cover established. A comparison will be made of the cost-effectiveness of soil removal versus a waste-in-place approach with subsequent post-closure monitoring.

The fourth closure technique to be evaluated is leaving the site as is. Efforts that might be employed to retard contaminant release include: tilling the site and adding fertilizer to foster further degradation of any waste residuals; maintaining the soil pH at 6.5 or greater to immobilize metals.

Work Plan

Work for this project will be conducted in two phases--(1) development of the site and (2) experimental work.

Phase 1 - Development of the Site

An active site, or portion thereof, will be selected to be used in the study. The experimental site will be of sufficient size to allow at least six smaller plots to be identified. These smaller plots will be isolated from each other by barriers. The barriers will not be made of any materials which might add chemical species to the soil or water and will not protrude above the ground so as to interfere with or change the normal wind direction.

A control plot will be set up on similar soils nearby that have not received waste. Background levels of contaminants in the soil and runoff water will be determined and compared with the levels from the experimental plots.

Four of the six experimental plots will have the following conditions: (1) left in the natural state, (2) vegetative cover, (3) removal of contaminated soil, placement of new soil, regraded, and vegetative cover established, and (4) capped like a landfill. The two remaining experimental plots will be tilled at regular intervals, and one plot will receive fertilizer.

Rainfall infiltrometers will be installed for use in determining the soil loss for each plot. Lysimeters will be used to determine the vertical transport of contaminants in the soil-pore water.

Phase 2 - Experimental Work

Soil loss and infiltration of water will be studied using either natural or artificial rainfall. In either or both cases, the procedures to be used and the advantages and disadvantages of these techniques will be described.

Runoff and infiltration water and soil losses will be analyzed for residual contaminants left in the soil. Individual classes of compounds will be determined. Soil cores will be taken from each plot and analyzed in a manner so as to determine the amount of residual inorganic and organic contaminants left in the soil and any vertical migration that might have occurred.

It is expected that a matrix of information will come from this experiment on the effects of surface treatments on runoff and infiltration waters and the potential for vertical migration of waste residuals.

PROPOSED CLOSURE EVALUATION FOR PETROLEUM RESIDUE LAND TREATMENT

The major objective of this study, conducted by the University of Oklahoma, is to determine the extent of migration of pollutants through the soil at closed oily waste land treatment facilities. In addition, the effect of land treatment on runoff quality, vegetation, and soil structure will be studied.

The contractor will develop an unsaturated zone monitoring plan in order to satisfy the objective of the study. The plan will include the use of soil cores and lysimeters, and based on site and waste specific conditions, will specify the number of soil cores and lysimeters to be used. The monitoring plan developed will represent the measurement tool for determining if contaminants in the soil will pose any future health or environmental problems. The study will attempt to resolve whether monitoring results serve as reliable indicators of potential environmental or human health problems.

Work for this project will be conducted in three phases: (1) site selection,

(2) monitoring program, and (3) correlation studies.

Phase 1 - Site Selection

The first phase of the project will be to secure three closed landfarming sites for the subsequent evaluations. Criteria for site selection will include:

(1) Time expired since site closure
  (a) recent exposure
  (b) minimum of 2 years
  (c) 5 years or longer

(2) Information available on site operation history; i.e., loading rates, characterization of applied residues, frequency of application, methods of operation, and other background information.

(3) Site and soil characteristics.

(4) Existence of similar soils representing background conditions.

Once the project study sites are selected and investigation arrangements are completed, a preliminary survey of the selected sites will be conducted to gather and organize pertinent information. Specific information desired includes:

(1) Time periods of site operation.

(2) Source, quantity, and characterization of residues applied on the site.

(3) Background information on soil characterization.

(4) Site operation procedures; i.e., frequency of residue application, management practices, fertilization practices, and monitoring practices.

(5) Historical site monitoring data.

(6) Use of site since closure.

(7) Adjacent land-use practices and planned site uses.

(8) Site map.

This information will provide a framework from which to evaluate subsequent site data to be collected.

Phase 2 - Monitoring Program

The contractor will develop an unsaturated zone monitoring plan for each site. The plan will be based on specific site criteria, waste types (if known), historical information on the site (i.e.—waste application method, application rate, frequency of tilling, etc.) and preliminary sampling by the contractor.

After the plan is established for each site, the contractor will take soil cores and install soil lysimeters. Soil cores will also be taken from nearby control plots which have not received wastes.

The constituents to be analyzed include polynuclear aromatic (PNA) compounds and heavy metals on the EPA list of hazardous compounds which potentially could be found in petroleum refinery sludges. In addition, total-cyanides and total-phenols concentrations will be measured. The soil core constituent analysis parameters are listed in Table 2.

TABLE 2. SOIL CORE CONSTITUENT ANALYSIS PARAMETERS

Antimony	Nickel
Arsenic	Benzanthracenes
Benzene	Benzopyrenes
Beryllium	Benzofluoranthene
Cadmium	Crysene
Chromium	Dibenzanthracenes
Copper	Indopyrenes
T-Cyanides	Selenium
Fluoranthene	Silver
Lead	Zinc
Mercury	T-Phenols

The results of sample analyses from the closed sites and their respective controls will be compared to determine what effects waste application has had on the quality of the soil and soil pore water. The contractor will statistically determine if significant differences exist between the experimental and control plots.

Phase 3 - Correlation Studies

Current closure regulations for land treatment facilities recognize that the disposal of a hazardous waste is a "crucial environmental and health problem which must be controlled." The monitoring approach mandated in the regulations is to provide a quantitative measure by which to evaluate realization of the basic objective. The proposed study tasks in Phase 2 will yield valuable information to evaluate the appropriateness of the monitoring approach. The contractor will attempt to resolve whether acceptable monitoring results can be correlated with adequate control of potential environmental and health problems and conversely. Correlation studies will be conducted to address this question.

The following correlation studies are proposed to be completed at each of the three sites:

(1) Statistical variation study - Determine statistical reliability of the monitoring plan developed for each site in describing site hazardous constituent concentrations.

(2) Runoff simulation - Simulate rainfall on an isolated area of each site to determine selected hazardous waste constituent concentrations in runoff samples.

(3) Agricultural impacts - Determine whether effects of land cultivation practices on closed sites will inhibit plant growth and result in significant heavy metal uptake.

(4) Soil tests - Evaluate alteration of physicochemical properties of the test site soils by the land treatment process.

(5) Deep core and soil pore water analysis - Determine whether vertical migration of hazardous constituents takes place.

The correlation studies are expected to yield quantitative answers to the following types of questions for closed sites:

(1) Do results from the monitoring plan developed for each site provide a statistically reliable measure of hazardous constituent concentrations and differences between background levels?

(2) Will plant growth on the sites be inhibited and result in high levels of uptake of hazardous constituents?

(3) Will runoff from the sites contain potentially hazardous concentrations of toxic constituents?

(4) Has the soil structure been so significantly affected by the land treatment process as to destroy its future usefulness?

(5) Do acceptable levels of hazardous constituents in the surface zone of the site insure safe levels of the same constituents in the deeper soil zones and groundwater at time of closure?

Answers to these types of questions will provide an indication as to whether "acceptable" monitoring results as defined in the regulations are in fact acceptable from the standpoint of human health and the environment.

REFERENCES

1. Berkowitz, Joan B., et al. Field Verification of Land Cultivation/Refuse Farming. Disposal of Hazardous Waste, In: Proceedings of the Sixth Annual Research Symposium, U.S. Environmental Agency, EPA-600/9-80-010, Cincinnati, Ohio 45268. pp. 260-273.

2. CONCAWE 1980. Sludge Farming: A Technique for the Disposal of Oily Refinery Wastes. Report No. 3/80. The Hague, Netherlands. 94 pp.

3. Huddleston, R. L. 1979. Solid-waste Disposal: Landfarming. Chemical Engineering, February 26, 1979. pp. 119-124.

LAND TREATING TANNERY SLUDGES
INITIATION OF A FIVE YEAR INVESTIGATION

Robert M. Lollar
Tanners' Council of America (14)
University of Cincinnati
Cincinnati, Ohio 45221

ABSTRACT

The main objective of this investigation is the characterization of the technical and the environmental aspects of the utilization of land treatment technology for treating tannery sludges. This five year project will assess the environmental impact of the application of two tannery wastewater sludges when applied to soil plots. The two sludges are the proteinaceous/lime rich unhairing (beamhouse) sludges and the trivalent-chromium containing sludges from the other portions of a full chrome-tanned cattlehide tannery.

The two sludges and a mixture thereof will be added to appropriate test plots annually at the end of each dry season. The grass grown on the test plots, the soil, the ground water and any leachate will be examined by analysis for various parameters but especially considering chromium partition. The site will be maintained under regular surveillance during the five-year period. The data will be assessed and appropriate site closure procedures will be developed. An overall goal is the development of data relevant to Best Engineering Judgement documents for land treatment facilities for tanning industry wastewater sludges.

A site has been leased in Santa Cruz County; its soil characteristics, geology and hydrology have been evaluated. A site plan for the specific location of the eight 0.2 hectare experimental plots has been developed, and run-off control facilities designed. These eight test plots, equipped with wells and other devices necessary to monitor the eight test plots, are being installed and will be given their initial sludge loading followed by grass seeding in December, 1980.

INTRODUCTION

The overall objective of this project is to determine whether land treatment technology is an environmentally sound method for the disposal of tannery wastewater sludges. Land treatment has been practiced for many years in many countries. Though the U.S. EPA/Corvallis has recently conducted greenhouse work on this topic, there has not been a definitive field study in accordance with applicable regulations. This project proposes a long-term program designed to provide the necessary data.

Specific objectives of the five year project are:

1. To assess potential adverse impacts of land treatment on various environmental sectors.
2. To measure sludge degradation rates of the sludges added.
3. To measure the accumulation and migration of contaminants in soil.
4. To optimize site design and operation (including closure).
5. To estimate the costs involved in a full-scale land treatment practice.

Since the project has the assistance of the following parties as subcontractors:

1. SCS Engineers (SCS): Engineering design, soil and plant monitoring.
2. University of California at Santa Cruz (UCSC): Surface and subsurface waters monitoring.
3. Salz Leathers, Inc. (Salz): Sludge delivery, contribution to project funds and technical liaison. Salz Leathers, Inc., is located in Santa Cruz, California. It has been in operation for 113 years and produces about 5 to 6 percent of the total yield of United States leather. Salz has also retained Weber and Associates as consultants; and Weber are especially involved in site selection and characterization.

EXPERIMENTAL PLAN

Wastewater Sludges

Wastewater sludge is generated at the Salz tannery at an overall level of approximately 50 wet metric tons (at 25 to 30 percent solids) per day, or 15,000 wet metric tons per year. These sludges are currently disposed of at a specially designed municipal landfill site, reflecting State of California requirements. Tannery wastewater sludges have been delisted under RCRA (1).

The tannery wastewater pretreatment system produces two different pretreatment sludges:

1. The dehairing wastewater sludge which results from the hair pulping (hair-burn) processes. It is rich in lime and proteinaceous residues resulting from the hair destruction process.
2. The tanning process wastewater sludges generated by Salz. This sludge is characterized especially by its content of trivalent chromium resulting from the tannage of the cattlehides in their conversion to leather.

Table 1 presents a representative analysis of these two sludges.

Although these wastewater sludges are generated separately at the Salz tannery, in many tanneries the wastewater pretreatment sludges originate from the overall wastewater flow. The experimental plan is designed to evaluate the disposal of the individual sludges and their mixture in the ratio generated in the Salz tannery.

Each of three sludges will be applied to individual test plots at two different sludge levels each successive year. Two sludge loading rates are planned, one at 336 Kg N per hectare (300 lb N per acre), an optimum level, and the other at 672 Kg N per hectare (600 lb N per acre), an excessive level.

Since there are three sludge types each applied at two different levels, six test plots are required. In addition, a control plot and an additional plot spiked with additional trivalent chromium are included. Hence, the test site will include eight experimental plots.

The total chromium loadings during the four years of annual application in the fall (late in the dry season) will be 1880 Kg per hectare (762 Kg per acre) in the plot to which the tanning process wastewater sludge is applied at the lower level. The plot to which the tanning process wastewater sludge is applied at the higher level will receive during the four years a total of 3760 Kg per hectare (1524 Kg per acre). These levels are below the limit of 4940 Kg per hextare (2000 Kg per acre) for a soil with a CEC greater than 15 meq per g (calculated from cumulative irrigation water standards for 10 year periods adopted by the FWPCA).

Site Plan

An 8 hectare (20 acre) site which lies within the Scott Creek valley in western Santa Cruz County, California, has been leased for the project by Salz

TABLE 1. CHEMICAL ANALYSIS OF SALZ SLUDGE**

Constituent	Dehairing Sludge (Hair-burn)	Tanning Sludge (Chrome)
Moisture	73.2%	73.1%
pH in Water	9.5	8.0
pH in 0.01M CaCl	9.8	8.1
Electrical Conductivity	5.5 mmhos/cm	7.1 mmhos/cm
Sodium Adsorption Ratio	7.7	3.8
Total Organic Carbon*	24.4%	22.8%
Total Kjeldahl Nitrogen*	3.8%	4.0%
Nitrate Nitrogen*	18.0 mg/kg	3.5 mg/kg
Ammonia Nitrogen*	123 mg/kg	106 mg/kg
Chromium*	49 mg/kg	52,500 mg/kg
Lead*	13 mg/kg	209 mg/kg

* Concentration data expressed on dry weight basis.

** Data supplied by SCS Engineers.

Leathers, Inc. The site is on a small, almost flat marine terrace remnant which lies between 107 m (350 ft) and 122 m (400 ft) in elevation; it is between 91m and 107 m above the floor of Scott Creek. The slopes at the site are generally 5 to 8 percent, increasing in some portions to 12 percent.

The site lies on a late Pleistocene marine terrace that has been formed in hard, poorly permeable, tertiary, mudstones. The test site is underlain by 9 to 14 meters (30 to 45 feet) of poorly consolidated sands and silts. Hand-auger core-hole logs indicate moderate-to-strong argilic "B" horizon soils present over the entire site. The site geology and hydrology is being evaluated in detail for later reference.

The six primary two tenths hectacre (0.5 acres) plots are placed on 5 to 10 percent slopes. The control plot, and the plot for the spiked trivalent chromium addition are adjacent to the six primary plots. Each of the eight plots is surrounded by a ditch-berm system to catch the surface runoff on the plots. The collected surface runoff is monitored and managed by clarifier-siltation pond energy dissipation systems. Lysimeters, and shallow and deep wells are installed to permit subsurface water monitoring.

Sludge Application and Seeding

The soil, after sampling, will be plowed or disced. The appropriate sludge application, augmented by potash and phosphate fertilizer nutrients as indicated, will then be placed on the plots and incorporated uniformly into the top soil. Native grass species (salt-tolerant and having high nitrogen requirement) will be seeded on the plots after sludge incorporation.

Monitoring

Monitoring will be maintained throuthout the contract period. Sludge analyses, soil and leachate analyses, plant analyses and ground water analyses will be accomplished.

Sludge sample analysis will include moisture, pH, electrical conductivity, and total organic carbon. The total nitrogen and the ammonia-N and nitrate-N distribution will be determined. Sodium adsorption ratio, total chromium and lead will also be measured.

The soil samples will be analyzed similarly. Furthermore, cation exchange capacity will be determined. The distribution of the chromium between the trivalent and hexavalent oxidation states will also be monitored.

The primary purposes of plant monitoring are to determine:

1. The growth response to tannery sludge
2. The nitrogen removal capacity of the sludges

The uptake and phyto-toxicity of chromium and salts are of secondary importance.

Shortly after seeding, the percentage and rate of seedling emergence from each plot will be observed during the emergence period. Differences in the plant density among the plots will be visually compared and photographically recorded. Plant tissues will be sampled and analyzed for total nitrogen, total chromium and lead.

The hydrological monitoring will be especially directed toward the possible leachate of nitrate nitrogen and total chromium into the ground water. The potential for appearance of hexavalent chromium in the leachate following organic matter decomposition will also be evaluated. Lead, electrical conductivity and pH of the ground water will also be monitored.

---

[1] Part XI. Environmental Protection Agency-Hazardous Waste Management System, Federal Register, Vol. 45 No. 212, Oct. 30, 1980.

INORGANIC HAZARDOUS WASTE TREATMENT. II

Warren J. Lyman
Arthur D. Little, Inc.
Cambridge, Mass. 02140

Gayaneh Contos
Versar, Inc.
Springfield, Va. 22151

ABSTRACT

This report describes an ongoing program to investigate selected processes for the treatment of inorganic hazardous wastes. A primary focus of the program is on wastes containing heavy metals; a secondary focus is on wastes containing organic as well as inorganic components. The report contains preliminary results from laboratory and small-scale pilot treatability studies on: (1) mixed acid wastes containing high levels of heavy metals plus some organic matter; (2) landfill leachate containing some industrial pollutants (heavy metals and organics); and (3) a heavy-metal containing sludge which is treated by high-gradient magnetic separation.

INTRODUCTION

Arthur D. Little, Inc., along with Versar, Inc. as a subcontractor, is currently in the final phase (Phase III) of an inorganic hazardous waste treatability study that was initiated in 1978 by the Solid and Hazardous Waste Division of MERL. A particular focus was on hazardous wastes disposed of in the municipal sector (i.e., off-site). Such wastes are often complex mixtures of wastes from various processes (and sometimes different plants) and are not usually amenable to material recovery. In Phase I a survey of potential treatment technologies was conducted. A total of 21 unit processes were eventually identified as being applicable to the treatment of inorganic hazardous wastes. In Phase II a screening process was used to narrow down the candidate list of treatment processes with the intent to eventually select four for in-depth study. Simultaneously we engaged in a search for available waste streams that could be used in our laboratory and pilot plant studies. The results of our Phase I and Phase II studies are described in more detail in a previous report (Lyman and Contos (3)).

The treatment processes and wastes selected for demonstration tests in Phase III were: (1) the treatment of mixed acid wastes, primarily from electroplating and metal finishing industries, by a dual-precipitation ($Ca(OH_2)$ plus Na_2S), filtration, and adsorption (powdered carbon) process; (2) the treatment of landfill leachates, containing some industrial contamination, by a dual-precipitation ($Ca(OH)_2$ plus Na_2S), filtration, and adsorption (powdered carbon) process; and (3) the treatment of a heavy-metal-contaminated sludge (primarily comprised of filter aid) by high gradient magnetic separation.

TREATMENT OF MIXED ACID WASTES

Waste Characteristics and Sources

The mixed acid wastes selected for study were obtained from a licensed hauler of hazardous wastes in New England. This hauler collects wastes from many of the small industries in this area and transports the wastes to treatment and disposal sites in other states. Aqueous wastes collected from electroplating and metal finishing plants are segregated into the following eight categories: (1) ammonium persulfate; (2) sodium persulfate; (3) electroless copper; (4) aqueous alkali (without NH_3); (5) aqueous alkali (with NH_3); (6) acid bath (without NH_3); (7) acid bath (with NH_3); and (8) cyanide bath. Wastes in categories 6 and 7 were chosen for study in this program, in part because they form a significant fraction of the wastes collected from these industries.

When a sufficient quantity of wastes in one category are on hand - typically about 19,000 liters (5,000 gal) - the hauler combines them (from individual drums) into one tank for transport to a treatment and disposal site. Two such batches - designated samples A and C - were sampled in Phase II and subjected to laboratory analysis and laboratory treatability studies. Four additional batches - designated samples F, G, H and I - were sampled (in 55-gallon drum quantities) for the Phase III laboratory and pilot-scale treatability studies.

The principal, non-aqueous component of these two wastes is a mixture of hydrochloric, sulfuric, nitric, and other acids. The acid wastes with and without NH_3 differ little except in their NH_3 content (about 10,000 mg/L (as N) vs 100 mg/L, respectively). The principal characteristics of the acids wastes are as follows:

- pH $\sim$ 0.5 to 1
- Heavy metal content $\sim$ 1,000 to 9,000 mg/L
- Principal heavy metals (in order): Ni, Cu, Cr, Aℓ, Fe, Mg, Sn, Pb, Zn, Mn, Co
- Dissolved solids $\sim$ 50,000 to 140,000 mg/L
- Suspended solids $\sim$ 30 to 10,000 mg/L
- NH_3 (as N) $\sim$ 120 to 17,000 mg/L
- Total organic carbon $\sim$ 3,900 to 5,300 mg/L
- Chemical oxygen demand $\sim$ 10,000 to 17,000 mg/L
- Principal anions: $C\ell^-$, $SO_4^=$, F^-, NO_3^-, $PO_4^{\equiv}$
- Toxic organics and chelating agents: present
- Color: green

Treatment Objectives

The primary treatment objective for these wastes is the removal of all hazardous components to the extent that the treated aqueous effluent could be safely discharged to a publicly-owned treatment works (POTW). Specific treatment objectives for each pollutant are difficult to define since federal regulations for hazardous waste treatment operations have not been set, and dilution ratios (at the point of discharge to the sewer) and local sewer ordinances (designed to protect the specific treatment operations at the POTW) may vary significantly from site to site. In spite of the above, we will be comparing the quality of the treated effluent with specific guidelines, including:

- Recommendations of the National Commission on Water Quality (NCWQ (4)) for pretreatment standards for electroplaters discharging to POTWs;
- U.S. EPA effluent limitations for existing sources in the electroplating point source category discharging to the POTWs (EPA (1));
- U.S. EPA options for effluent limitations for the metal finishing point source category (EPA (2)); and
- Other studies indicating what levels of toxic chemicals should not be discharged to POTWs.

These guidelines tend to limit the effluent concentrations of various heavy metals to about 1 mg/L each, with most limits being in the range of 0.6 to 4 mg/L. A total heavy metal limitation is specified in one case (EPA (1)); this total ranges from about 7 to 20 mg/L depending on the volume of waste generated, the type of sample collected, and the type of treatment used. Because of the complex and variable nature of the acid wastes chosen for this study -- and because of their relatively small volume compared to total POTW influent flows -- we do not expect that the cited guidelines should or could be used as an absolute scale for determining treatment effectiveness.

Secondary treatment objectives for this study included: (1) the development of a process that was not only simple and economical to operate, but also highly effective and capable of handling a highly variable input waste; and (2) an investigation of the potential for separating and recovering selected heavy metals.

The Treatment Process

The treatment process used for the mixed acid wastes was designed to neutralize the acids, and to effect a high removal of heavy metals, toxic organics and some anions. The key unit operations in this design are: (1) heavy metal precipitation via addition of $Ca(OH)_2$ and Na_2S; (2) adsorption of organics with powdered activated carbon; and (3) filtration for the removal of both the metal precipitates and powdered carbon. In addition, the process was designed to (hopefully) overcome a number of potential problems, including:

- The fact that the minimum solubilities for the heavy metals present are at different pH values, which values are difficult to predict because of the complexity and variability of the solution. Thus, the selection of just one "optimum" pH for removal of precipitated metals - an optimum that would be used for all waste batches - would be unlikely to effect a consistently high removal for all heavy metals.
- The fact that the high ionic strength of the waste (≥ 1) was likely to result in soluble ion pairs, thus further complicating the precipitation of heavy metals.
- The fact that metal complexing agents (NH_3, organic acids, chelates (e.g., EDTA)) were likely to be present, also interfering with metal precipitation.
- The possibility that too rapid a rise in the pH (during the neutralization process) could lead, temporarily, to a highly supersaturated solution which, in turn, could lead to the formation of very fine precipitates that would be difficult to filter out.
- The fact that some organics present were acidic in nature and were not likely to strongly sorb to carbon at a pH where a significant fraction was in the dissociated form.

The basic steps in the treatment process are:

(1) The slow addition of (powdered) $Ca(OH)_2$ to the mixed waste, and periodic filtering, as the pH is raised from its initial value of 0.5-1 to about pH 8. (In laboratory tests, the reaction mixture was filtered after each unit increase in pH, in subsequent pilot plant tests, the filtration was typically once every two pH units.) The waste was, at times, filtered before any $Ca(OH)_2$ was added.

(2) The addition of powdered activated carbon at two different points in the filtration process within the pH range of 6 to 10. (A typical carbon dosage was 3 g/L (total) for a waste.)

(3) The slow addition of Na_2S within the pH range of 8 to 10, again with periodic filtering. (The amount of Na_2S used generally resulted in a further pH rise of 1/2 to 3 pH units.)

(4) The slow addition of $Ca(OH)_2$, again with periodic filtering, until a pH of about 12 is attained.

(5) The back neutralization of the waste with HCℓ from pH 12 to a value in the range or 7 to 10.

Steps 1, 3 and 4 are designed to maximize the removal of heavy metals. The slow addition of reagents should prevent excessive supersaturation. The periodic filtering should take advantage of the minimum solubility of each heavy metal, wherever it lies within the pH range of 1 to 12. And the addition of the sulfide reagent (Na_2S) is designed to effect a higher degreee of heavy metal removal than is possible by hydroxide precipitation alone. In addition, this reagent should reduce any hexavalent chromium present and allow it to be precipitated. Finally, in step 4, the raising of the pH to nearly 12 was expected to help break certain heavy metal complexes which would be stable (and soluble) at lower pH values.

The use of powdered activated carbon (step 2) was designed to avoid the common problems and associated expenses of fixed-bed granular carbon systems. These problems include: (1) the necessity for more complex systems (additional tanks, filter beds, pumps, etc.); (2) filter bed clogging and/or the necessity for frequent backwash; (3) higher costs of granular carbon and/or the necessity to regenerate the carbon. The powdered carbon in our process is not intended to be recovered for regeneration.

Laboratory Treatment Tests

One of the more important laboratory tests conducted was a trial run of the stepwise precipitation/filtration process described in the previous subsection. Five acid waste batches were tested in this fashion; for sample C a 25-mL test volume was used (obtained from a 1-liter sample provided by the waste hauler); for samples F, G, H and I a 1.5-L test volume was used (obtained by sampling a 55-gal. drum of the waste provided by the hauler).

Figure 1 shows the amount (dry weight) of precipitate removed by filtration during this treatment process. Note that the only common feature of the individual figures is the high solids removal between pH 1 and 2. These solids are made up primarily of calcium and sodium salts; crystals of $Na_2SO_4 \cdot 10H_2O$ were identified in one sample from a measurement of the crystal's refractive index. The total amount of solids removed during the treatment process ranged from 60-80 g/L for the three acid wastes "without" ammonia (C, G, I), and from 130-160 g/L for the two acid wastes "with" ammonia (F, H).

Figure 2 provides neutralization curves for these same five wastes. The amount of base (and acid) used is given in units of gram-equivalents used per liter of waste. (One gram equivalent of a base will release one mole of OH^- ions.) These curves point out additional differences between the acid wastes "with" (F, H) and "without" (C, G, I) ammonia. The latter only require about one gram equivalent of base for the treatment process while the former require as much as three to five gram equivalents. In addition, the two wastes "with" ammonia both show a sharply rising curve in the region of

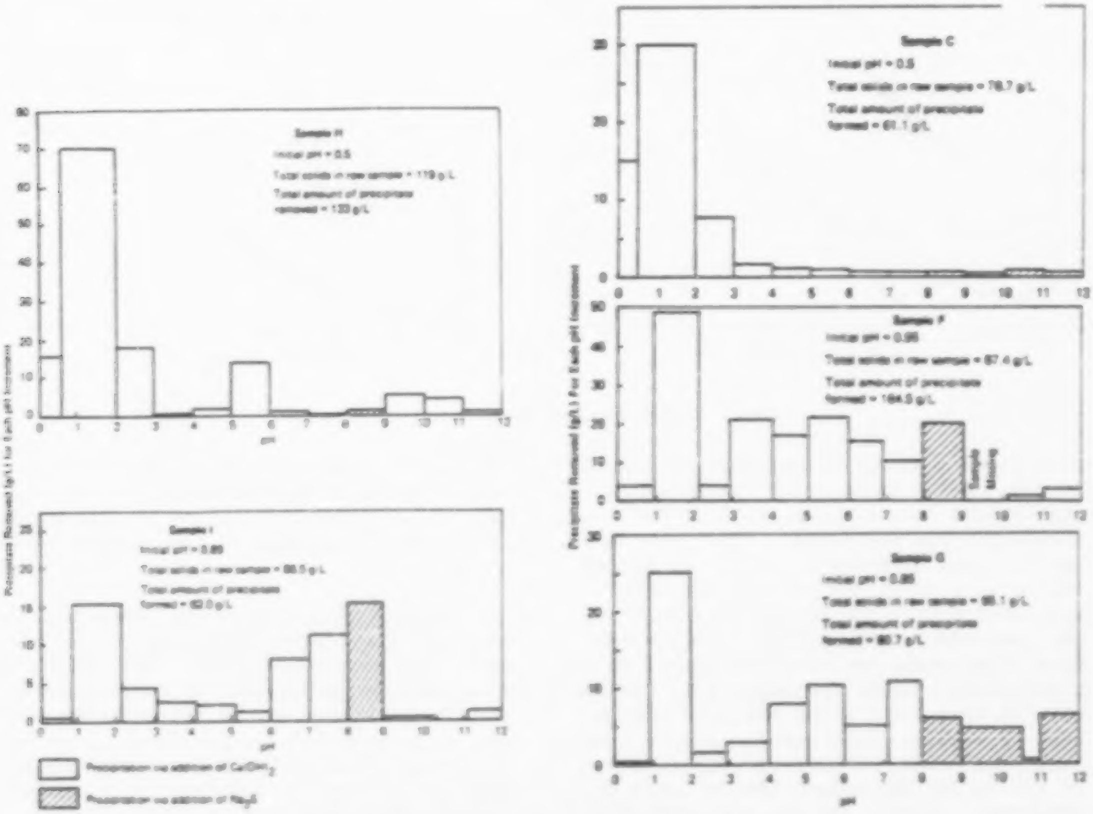


FIGURE 1 PRECIPITATE REMOVAL VS. pH FOR ACID PLATING WASTES

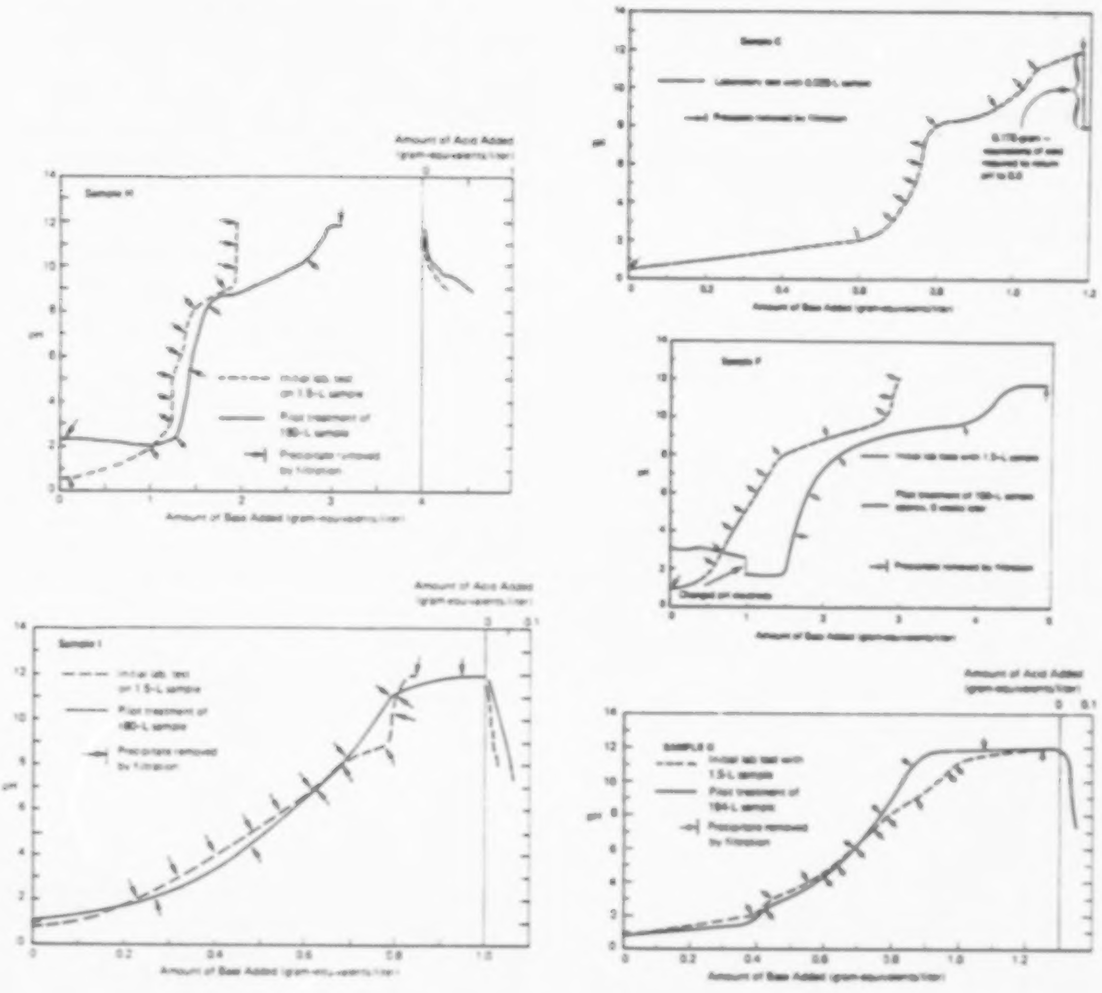


FIGURE 2 ACID AND BASE REQUIREMENTS FOR TREATMENT OF ACID WASTES

pH 2 to 8, a factor which makes pH control in this region difficult. These wastes also showed - when the results of the laboratory and pilot plant tests are compared - some anomolous behavior at low pH. The initial pH of the pilot plant waste was about 2 pH units higher than that of the laboratory sample taken from the same drum a few weeks earlier; and the pH of the pilot plant samples decreased with the addition of base until about one gram equivalent of base had been added. Sample handling procedures, leading to higher losses of NH_3 in the laboratory samples, may be involved. Overall though, the neutralization curves from laboratory and pilot plant runs agree relatively well; this implies that laboratory neutralization curves can be used as a fairly accurate predictor for the (batch) treatment of much larger volumes of waste.

Figures 3 and 4 show the removal of the most prevalent heavy metals as a function of pH in two laboratory tests. Both show aluminum and iron being removed at relatively low pH (1-5) and most of the chromium coming out at intermediate values (3-7). The major difference lies in the behavior of copper and nickel. In waste F (Figure 3), which contains high levels of ammonia, the two metals act similarly; small amounts are

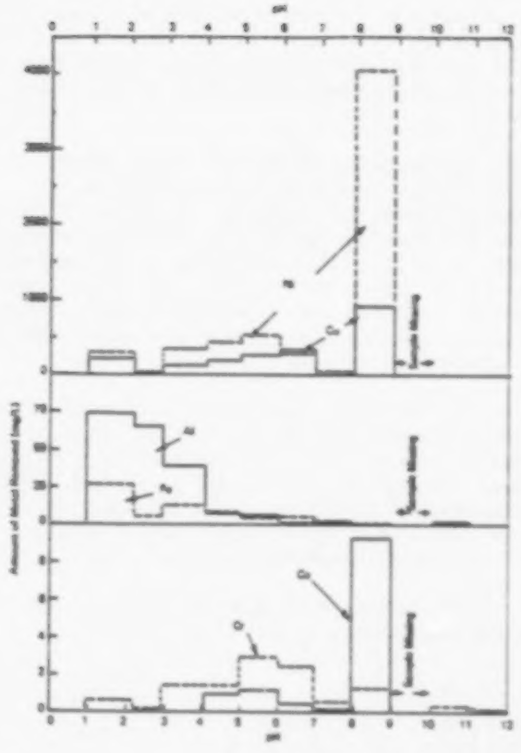


FIGURE 3 REMOVAL OF METALS VS pH FOR ACID WASTE F (LABORATORY TEST)

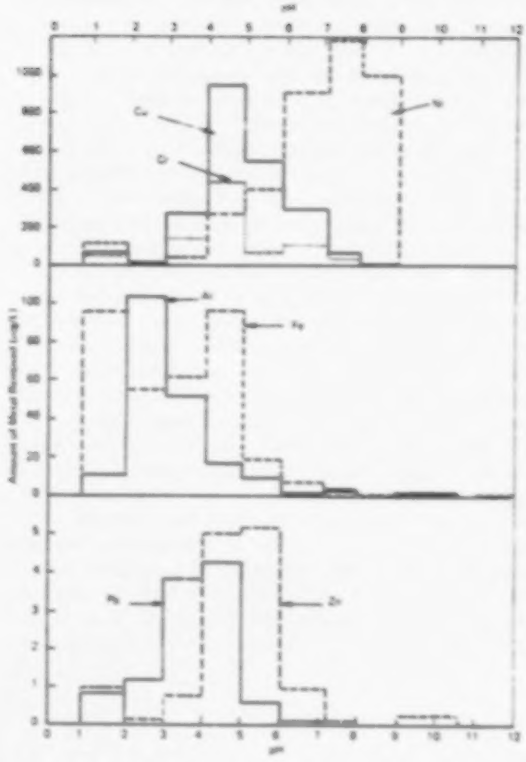


FIGURE 4 REMOVAL OF METALS VS. pH FOR ACID WASTE G (LABORATORY TEST)

removed in the 1-7 pH range and a peak is seen in the pH 8-9 increment. In waste G (Figure 4), which contains relatively little ammonia, the copper comes out earlier than the nickel. For this waste there would appear to be some potential for the separation (and recovery) of nickel; other metals are concentrated in the precipitates formed below pH 6 while the nickel is concentrated in the precipitates formed above pH 6.

Table 1 shows the results of laboratory carbon adsorption tests. The data show that even high doses of the carbon, up to 8.5 g/L, could remove only about 30% of the total organic carbon (TOC) and that the pH at which the carbon was added was not very important (at least for TOC removal). Fairly high removals of oil and grease were seen under all conditions.

The treatment effectiveness (for heavy metals removal) seen in these laboratory tests is discussed later on in conjunction with the pilot plant treatment tests.

Pilot Plant Treatment Tests

Small-scale pilot plant treatment tests were carried out with four acid wastes (samples F, G, H and I) using the treatment

TABLE 1. LABORATORY TESTS WITH POWDERED ACTIVATED CARBON

Sample	Adjusted pH	Carbon Dose (g/L)	Analysis of Filtrate: TOC (mg/L)	Analysis of Filtrate: Oil and Grease (mg/L)
F	5.0	0 1.7 8.5	3700 4100 2960	93 < 1. 1.
G	3.0	0 1.7 8.5	3600 3500 2530	62 2. 2.
F	5.0 followed by 8.0	5.1 3.4	2700	2
G	5.0 followed by 8.0	5.1 3.4	2510	1

process described previously. A schematic diagram of the treatment system is shown in Figure 5. A 266-liter (70 gal.) plastic barrel was used as the reaction tank. In each test about 200 liters of waste (the complete contents of the 55-gal. drum obtained from the waste hauler) was used. The filters used were non-woven fabric filter bags (nominal pore diameters of 5 to 10 microns (20 microns for sample F)) held in vertical cylinders. The original plan called for recirculation of the waste through these filters and back to the reaction tank. However, the large volume of solids (precipitates, carbon and filter aid) frequently built up a substantial back pressure in the filters (15-30 psi) resulting in recirculation flow rates (~2-15 liters/min.) that were too low to be effective. Thus, when filtration was desired - about every 2 pH units - the complete contents of the reaction tank was pumped through the filters to a collection barrel; the filtrate was subsequently pumped back to the reaction tank for further treatment. Filter aid (diatomaceous earth) was used for all filtration steps except those during the treatment of sample F. Some problems with solids retention had been noticed in this initial run; the use of filter aid and more closely woven filter bags nearly eliminated the problem in subsequent runs.

The specific treatment regime given each of the four acid wastes is shown schematically in Figure 6. Samples of the raw and treated waste (for pollutant analyses) were collected according to a standard protocol just prior to, and just after, the pilot treatment run. In some cases, intermediate samples (for metals analyses) were collected after each filtration step.

The chemical usage associated with these pilot treatment runs is shown in Table 2; the values are in units of grams of chemical used (mL for HCℓ) per liter of waste. These numbers are important since chemical costs are expected to be a significant fraction of the total treatment costs.

The amount of sludge generated during this treatment process is significant.

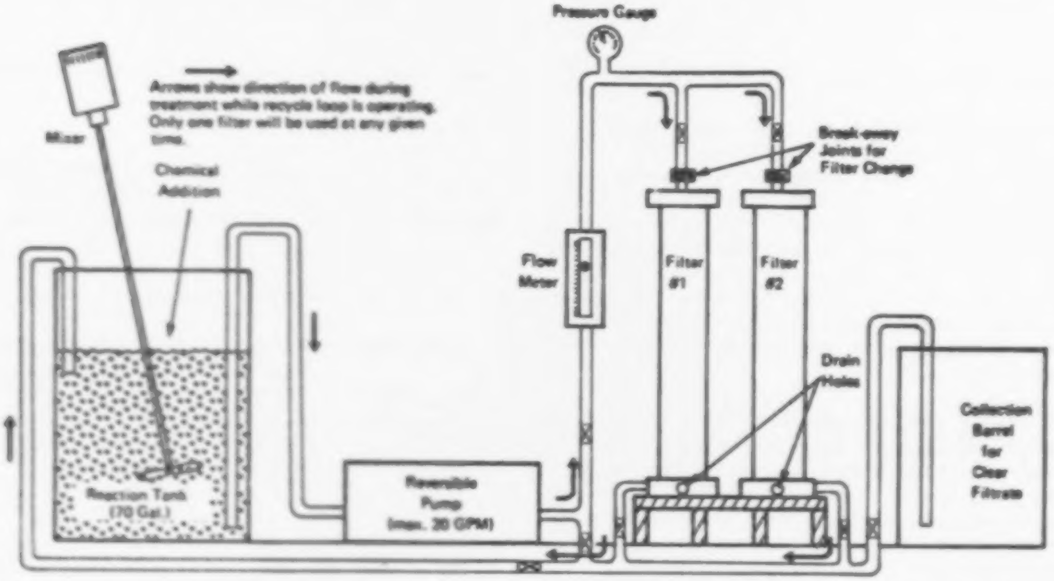

Pressure Gauge
Arrows show direction of flow during treatment while recycle loop is operating. Only one filter will be used at any given time.
Mixer
Chemical Addition
Break-away Joints for Filter Change
Flow Meter
Filter #1
Filter #2
Drain Holes
Collection Barrel for Clear Filtrate
Reaction Tank (70 Gal.)
Reversible Pump (max. 20 GPM)

FIGURE 5 SCHEMATIC DIAGRAM OF PILOT TREATMENT SYSTEM

TABLE 2. CHEMICAL USAGE ASSOCIATED WITH PILOT PLANT TREATMENT RUNS

Acid Waste	$Ca(OH)_2$ (g/L)	Na_2S (g/L)	HCℓ (~37%) (mL/L)	Powdered Carbon (g/L)	Filter Aid (g/L)
F (with NH_3)	124	69.4	(42)[a]	2.6	Not Used
H (with NH_3)	97.8	16.1	46.2	4.0	11
G (no NH_3)	36.4	3.6	4.3	3.1	10
I (no NH_3)	31.9	3.6	8.4	3.5	10

a. Calculated from laboratory data.

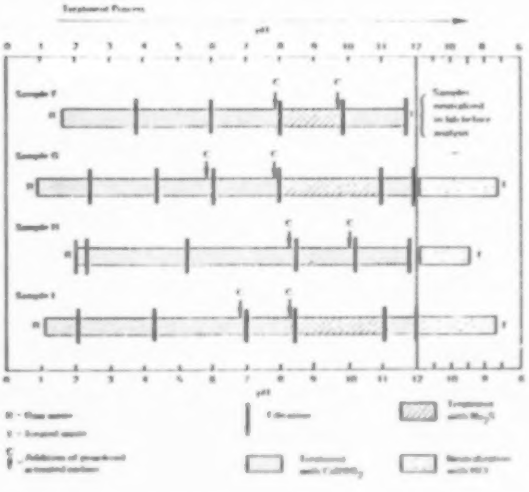


FIGURE 8. SUMMARY SCHEMATIC OF PILOT PLANT TREATMENT OF MIXED ACID PLATING WASTES

TABLE 3. ESTIMATES OF SLUDGE VOLUME GENERATED DURING TREATMENT

Acid Waste	Amount of precipitate formed in lab. tests (g/L)[a]	In pilot tests added: Powdered carbon (g/L)[a]	Filter aid (g/L)[a]	Sludge volume (cm^3/L) if sludge contains:[b] 50 wt. % water	75 wt. % water
C	61.1	--[c]	--[c]	89	210
F	164	2.6	--[d]	240	580
G	80.7	3.1	10	140	330
H	133	4.0	11	220	510
I	62.3	3.5	10	110	260

a. Values are grams (dry weight) per liter of waste. Densities of these materials assumed to be: (1) precipitates, 2.2 g/cm^3; (2) powdered carbon, wet density of 1.6 g/cm^3; (3) filter aid, wet density of 1.5 g/cm^3.

b. Values are cm^3 of (wet) sludge generated per liter of raw waste.

c. No pilot treatment tests carried out on sample C.

d. No filter aid used with sample F.

Table 3 provides estimates (the exact amounts were not measured) of both the weight and volume of sludge generated. The acid wastes with ammonia (F, H) provide the worst case. About 150-170 g (dry wt.) of sludge is produced for each liter of waste treated. If this sludge was only dewatered to 25 wt.% solids then 510-580cm^3 of sludge are generated per liter of waste, i.e., the volume of hazardous wastes has only been reduced by less than one half! Dewatering to 50 wt.% solids produces 220-240 cm^3 of sludge per liter of waste. The acid wastes without ammonia generate about one-half the sludge generated by the wastes with ammonia.

Preliminary Results

Pre- and post-treatment pilot plant samples were analyzed for: (1) over 20 metals; (2) specific organics (GC or GC-MS); (3) anions; and (4) conventional parameters. At present we can only report some of the metal data; other items will be discussed qualitatively.

The degree of metals removal achieved in the pilot runs is shown by the data in Table 4. In general, very high removal efficiencies were obtained in spite of the potential problems mentioned previously. A comparison of the Final concentrations with various EPA and NCWQ limitations for discharges to POTWs indicates relatively few problem areas, although it is apparent that these limitations could not be strictly met. Maximum Final concentrations - some of which exceed EPA limitations for

TABLE 4. CONCENTRATION OF HEAVY METALS (mg/L) IN INITIAL AND FINAL SAMPLES FROM PILOT PLANT TREATMENT OF ACID WASTES

	Waste F		Waste H		Waste G		Waste I	
Metal	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Aℓ	166	4.0	88	11	128	< 0.7	6.9	< 0.7
As[a]	260[a]	6[a]	780[a]	12[a]	6.[a]	1.[a]	610.[a]	14.[a]
Ba	1.7	0.5	1.2	2.9	0.8	0.8	0.4	1.1
Be	0.011	< 0.005	0.28	< 0.01	0.172	< 0.003	0.010	< 0.003
Cd	< 1	< 1	3.5	< 0.7	0.7	0.2	0.9	0.3
Co	14.3	< 0.5	0.6	< 0.5	1.4	< 0.1	2.6	< 0.1
Cr	3.39	0.08	93.5	< 0.08	689	4.96	40.9	1.28
Cu	2000.	1.73	19.0	0.09	1970	2.04	1050	2.07
Fe	72	2	42	< 2	165	2.4	262	3.0
Hg[a]	210.[a]	2.4[a]	510[a]	0.4[a]	0.2[a]	0.4[a]	0.4[a]	0.1[a]
Mg	48.4	< 0.1	36.3	1.3	100	0.8	4.3	1.5
Mn	2.2	< 0.1	1.9	< 0.1	1.75	0.23	1.85	0.22
Mo	< 1.	< 1.	< 3.	< 3.	< 0.6	< 0.6	< 0.6	< 0.6
Ni	6100.	8.7	1960	1.3	3180.	0.61	5620.	3.39
P	313.	< 1.	1760	< 5	2350	364.	1170.	871.
Pb	60.	< 0.5	132	0.15	8.00	< 0.20	18.5	< 0.2
Se[a]	10[a]	10[a]	11[a]	3.6[a]	4900.[a]	< 2.[a]	48[a]	19[a]
Sn	190	2.8	89	0.5	130.	1.	12.	0.2
Sr	0.39	0.68	0.12	0.53	0.52	0.52	0.03	0.47
Ti	3.39	< 0.05	< 0.1	< 0.1	0.28	< 0.03	0.37	< 0.03
Zn	3.90	0.35	26.5	< 0.2	5.89	0.25	13.7	< 0.05
Zr	2.2	< 0.5	0.5	< 0.5	< 0.1	< 0.1	0.3	< 0.1

a. Values for As, Hg and Se are in μg/L.

electroplating/metal finishing shops - for a few metals were: Aℓ, 11 mg/L; Cr, 4.96 mg/L; Cu, 2.07 mg/L; Fe, 3 mg/L; Ni, 8.7 mg/L; Pb, ≤0.5 mg/L; and Zn, 0.35 mg/L.

It is worth noting that the degree of metal removal was essentially the same in the pilot plant runs as it was in our preliminary laboratory tests; this was in spite of the fact that the latter had better pH control, more frequent filtering and finer filters. The removal efficiency (for total metals) of the laboratory and pilot plant tests are compared in Table 5.

Total heavy metals in the treated waste are seen to be in the range of about 10-30 mg/L when data for Ba and Sn are added in. This would not appear to be an unreasonable level for the discharge of relatively small volumes to a POTW by a hazardous waste treatment operation.

Initial laboratory analyses for this treatment operation have shown high removal efficiencies for F^- and $PO_4^{\equiv}$ (>90%), good removal of $SO_4^{=}$ (~90%), and some removal (~30%) of NO_3^-. Levels of $C\ell^-$ are increased due to the addition of $HC\ell$. Preliminary

TABLE 5. COMPARISON OF METALS REMOVAL IN LABORATORY AND PILOT PLANT RUNS

	Waste F		Waste H		Waste G		Waste I	
	Lab	Pilot	Lab	Pilot	Lab	Pilot	Lab	Pilot
Total Initial Metals:[a]	7567	8478		2407	7618	6881		7022
Total Final Metals:[a]	$\leq$21.2	$\leq$21.3		$\leq$26.4	$\leq$9.9	$\leq$13.7		$\leq$14.0
% Removal of Metals	$\geq$99.7	$\geq$99.7		$\geq$98.9	$\geq$99.9	$\geq$99.8		$\geq$99.8

a. Values in mg/L. Total is for Al, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sr, Ti, Zn, Zr. Values for As, Ba, Hg, Se, and Sn excluded since no analyses were done on samples from laboratory tests. P and Be also excluded.

data from our organics analyses (primarily for volatile compounds) have shown high removal efficiencies for the hydrophobic compounds (e.g., the volatile priority pollutants) and moderate to low removal efficiencies for the hydrophylic compounds (e.g., alcohols, esters, ketones, acids).

The aqueous effluent from this treatment process is essentially a concentrated salt solution comprised principally of Na^+, Ca^{++}, K^+, $C\ell^-$, NO_3^-, and $SO_4^=$ ions, and some soluble organic solvents (alcohols, ketones, esters, etc.) The range of values found (for samples F, G, H, I) for dissolved solids (DS), total organic carbon (TOC), chemical oxygen demand (COD), and 5-day biochemical oxygen demand (BOD) were as follows:

Parameter	Effluent Conc. (mg/L)	Average % Reduction
DS	60,000-120,000	30
TOC	1,400-3,300	40
COD	4,000-12,000	10
BOD	500-4,600	Increase

The four samples showed the following ranges for the principal metal cations: Na, 11,000-30,000 mg/L; Ca, 2,800-4,000 mg/L; and K, 4-310 mg/L. The principal inorganic anion is $C\ell^-$. The increase in the BOD noted above is presumably due to the removal (in the treatment process) of toxic pollutants that inhibited biochemical activity in the raw waste.

TREATMENT OF LEACHATES

Waste Characteristics and Sources

Four different leachates were investigated in this program. The four sites are briefly described below. Diagrams are provided in Figure 7.

Site A - A municipal landfill for an old city in New England currently accepting 150-200 tons of refuse per day. Industrial hazardous wastes may have been placed in this site in the past; current rules have excluded such wastes for several years. A sample of leachate (diluted with groundwater) was obtained from a sump in a nearby municipal building.

Site B - A municipal landfill in New England currently accepting about 150 tons of refuse per week. No hazardous wastes have ever knowingly been disposed of at this site. The site is about five years old and has built up a refuse mound about ten feet deep. Cones in the base of the landfill allowed pure leachate (undiluted by groundwater) to be collected.

Site C - A municipal landfill for a New England city with a population of nearly 40,000. Landfilling at this site started about 1960; about 32,000 tons/yr. of refuse are currently disposed here. Hazardous industrial wastes are not allowed. Samples were collected from the surface of a sump (serving as a lift station) in a leachate removal system. The samples are diluted by groundwater and may be more representative of "old" leachate (overlying material > 5 years old) than "new" leachate.

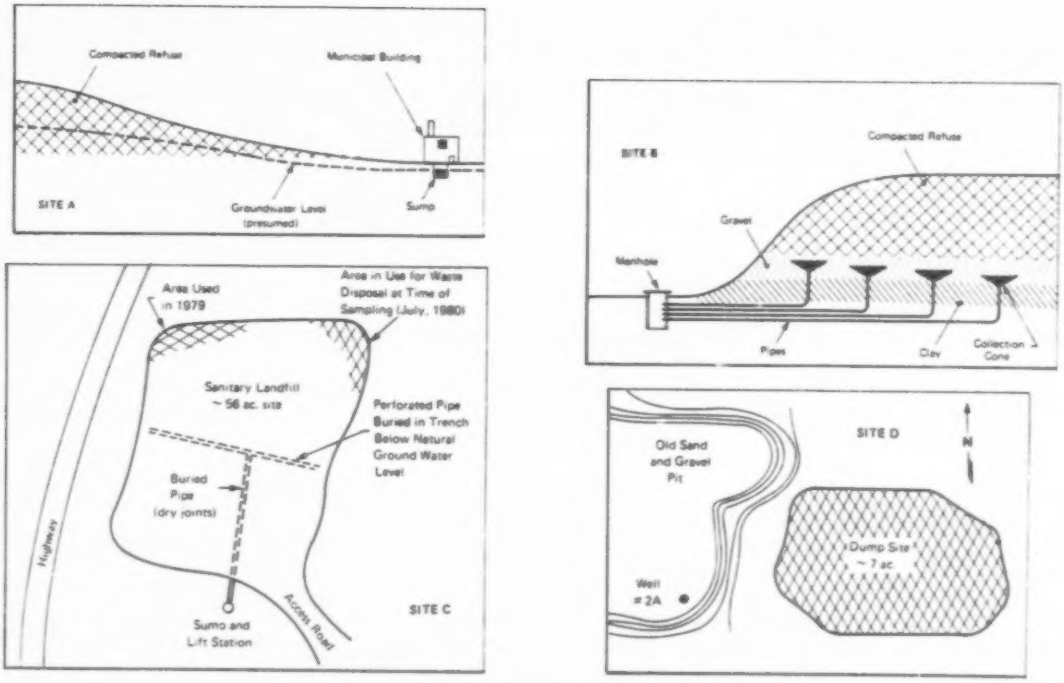

Compacted Refuse
Municipal Building
SITE A
Groundwater Level (presumed)
Sump
SITE B
Compacted Refuse
Gravel
Manhole
Pipes
Clay
Collection Cone
Area Used in 1979
Area in Use for Waste Disposal at Time of Sampling (July, 1980)
Sanitary Landfill ~ 56 ac. site
Perforated Pipe Buried in Trench Below Natural Ground Water Level
Buried Pipe (dry joints)
Highway
Sump and Lift Station
Access Road
SITE C
Old Sand and Gravel Pit
SITE D
N
Dump Site ~ 7 ac
Well # 2A

FIGURE 7 SCHEMATIC OF LEACHATE COLLECTION SITES

Site D - An unauthorized chemical dump site in New England. The site was an old sand and gravel pit into which construction and demolition debris, and chemicals (some in drums), were placed. Over 1300 drums (almost all 55-gal.) have been removed from the surface of the site. Samples were collected from a monitoring well about 50 m. west of the dump site.

About 230 liters of leachate was collected form both sites A and C; and 460 liters from both sites B and D. The wastes were collected and held (several weeks) in polyethylene-lined 55-gal. drums. The general characteristics of these leachates are described by the data in Table 6. The leachates from Sites B and D had very strong odors.

Treatment Objectives

The primary treatment objective for these leachates is the removal of all hazardous components to the extent that the treated aqueous effluent could be safely discharged to a POTW or subjected to biological treatment in other ways. In particular we wanted to effect a high degree of heavy metals and toxic organics removal. Since our primary interest was in leachates contaminated with industrial hazardous wastes, portions of two of the leachates that were from relatively clean municipal landfills (Sites B and C) were spiked with known quantities of seven heavy metals (Co, Cu, Ni, Zn, Pb, As and Cr) and seven organics (benzene, chlorobenzene, phenol, p-chlorophenol, toluene, naphthalene, and trichloroethylene)

TABLE 6. GENERAL CHARACTERISTICS OF THE LEACHATES USED[a]

	Site A	Site B	Site C	Site D
pH (units)	7.2	6.5	6.7	5.6
Color	rusty	rusty	rusty-pink	blackish
Suspended Solids	70	605	120	120
Dissolved Solids	465	6700	1100	2560
Ammonia Nitrogen as N	2.6	350	70	15
Total Organic Carbon[b]	18	2700	92	2400
Chemical Oxygen Demand	80	7400	180	7200
Biochemical Oxygen Demand[c]	25	3600	230	4710
Oil and Grease	<5	165	d	100
Conductivity (micromho/cm)	700	7880	d	d

a. All values except pH and conductivity are in mg/L.

b. Non-volatile TOC.

c. Five-day BOD.

d. Not analysed.

in order to simulate a more polluted leachate. Unspiked portions were also treated.

The Treatment Process

The treatment process used for the leachates - like that used for the acid wastes - was designed to effect a high removal of heavy metals, toxic organics and some anions. The key unit operations were, as before: (1) heavy metal precipitation via addition of $Ca(OH)_2$ and Na_2S; (2) adsorption of organics with powdered activated carbon; and (3) filtration for the removal of both metal precipitates and carbon.

No biological treatment (for the removal of BOD and COD) was employed. If the treated leachate from the chosen process could be easily discharged to a POTW (by sewer connection or truck transport), then this would be one way to economically add biological treatment. Alternatively, leachate recycle (via spray irrigation) through the landfill could be used to effect biological treatment at many sites. It was not practical in this program to simulate either of these alternatives in our treatment regime.

The chosen treatment process was chosen, in part, to allow relatively simple and economical, on-site (pre)treatment of leachate. It would hopefully overcome any metal-complexation problems and be generally applicable to a variety of leachates.

The basic steps in the treatment process are:

(1) The addition of HCℓ to acidify the leachate to pH 3-5 and the subsequent addition of powdered activated carbon at this pH. The carbon is removed by filtration. (The initial pH lowering is intended to reduce the degree of dissociation of organic acids and thus increase the amounts that would be removed by the carbon.) This step was not used with the Site D leachate.

(2) The addition of (powdered) $Ca(OH)_2$ to the mixed waste raising the pH to about 8; one or two filtrations are used over this pH range. An additional dose of carbon is added and then removed with the first filtration in this step. The Site D leachate started with the sequential addition and filtration of three doses of the powdered carbon.

(3) The addition of a small amount of Na_2S near pH 8, raising the pH from 0.5-1 units (i.e., to 8.5-9).

(4) The slow addition of additional $Ca(OH)_2$ with one or two additional filtration steps, until pH 11-12 is reached (pH 10 for the Site D leachate).

(5) Back neutralization with HCℓ to about ph 7.

The rationale for steps 2-5 is similar to that previously described for the acid wastes.

Laboratory Treatment Tests

Trial runs of the step-wise precipitation/filtration process were carried out in the laboratory for each of the four leachates. Sample volumes were 1.5 liters in each case. Figure 8 shows the amount (dry weight) of precipitate removed at each filtration step. Note that none of the diagrams show any similarity to each other. The neutralization curves for these leachates (not shown) also indicate a significant difference in their behavior during the treatment process.

Laboratory treatment tests with the powdered activated carbon, using TOC and oil and grease analyses, were inconclusive. As with the acid wastes, good removal of oil and grease but poor removal of TOC was apparent irrespective of the pH. The TOC in the Site D leachate was, for example, reduced from about 2300 mg/L to only 1600 mg/L after the addition of 10 g/L of carbon. Essentially the same results were obtained at pH 6.2 and 4.0

Pilot Plant Treatment Tests

Small-scale pilot treatment tests were carried out with the four leachates using the process described above. The treatment system was the same as was previously described for the acid wastes (Figure 5). About 200 liters of waste were used in each run. Filter aid (diatomaceous earth) was used in all filtration tests. The filter bags were eigher 5 or 10 micron nominal pore diameter.

Two leachates (Sites B and C) were treated in duplicate runs, one with and one without the heavy metal and organics spikes mentioned previously. The specific treat-

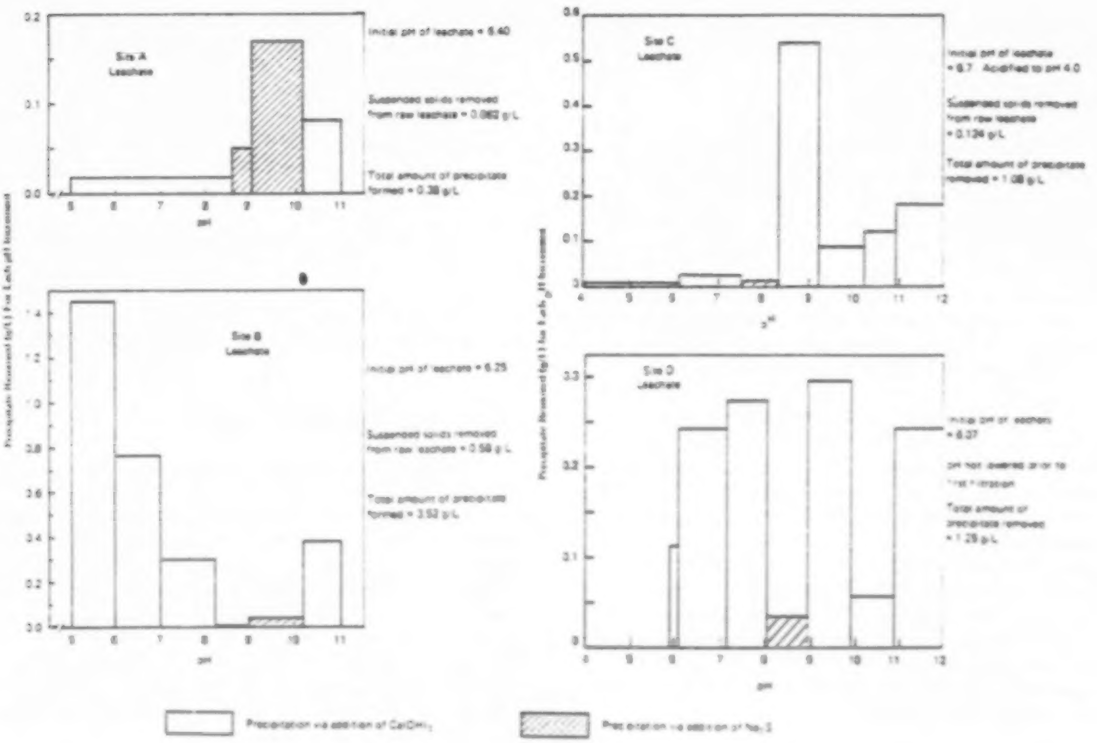


FIGURE 8 PRECIPITATE REMOVAL VS. pH FOR LEACHATE SAMPLES AFTER ACIDIFICATION TO pH = 5

ment regime for each of these wastes is shown schematically in Figure 9. Samples of the raw and treated wastes (for pollutant analyses) were collected according to a standard protocol just prior to, and just after, the pilot treatment runs. The chemical usage with these runs (important in the estimation of treatment costs) is shown in Table 7. The estimates of the amounts of sludge generated during the treatment process are shown in Table 8. The dry weight of the metal precipitates formed is less than the weight of either the filter aid or carbon added, and the total solids generated is in the range of 8-20 (dry wt.)/liter. Dewatering to 50 wt. % solids would produce between 13 and 31 cm^3 of sludge per liter of waste.

Preliminary Results

Pre-and post-treatment pilot samples were analyzed for: (1) over 20 metals; (2) specific organics (GC or GC-MS); (3) anions; and (4) conventional parameters. At present we can only report some of the metal data.

The data in Table 9 show that heavy metal concentrations in the four leachates were generally quite low except for Fe, Mg, and Mn. It would be difficult to determine from these data if industrial heavy metal wastes had ever been disposed of at these sites; only the Ni content at Site D appears to be suggestive of industrial contamination. The treatment process gave good removals for all of these metals. This is seen especially in the spiked pilot plant runs (Sites B and C) where known quantities of Co, Cr, Cu, Ni, Pb, Zn and As were added. The removal efficiencies for most of these metals in the spiked runs was over 98%. However, the removal efficiency for copper was only about 90% and final values of about 1 mg/L resulted. Complexation with naturally occuring organics may have been involved.

Sludge Treatment Via High Gradient Magnetic Separation

Currently, the typical treatment of industrial wastewaters that contain toxic metals includes the chemical precipitation

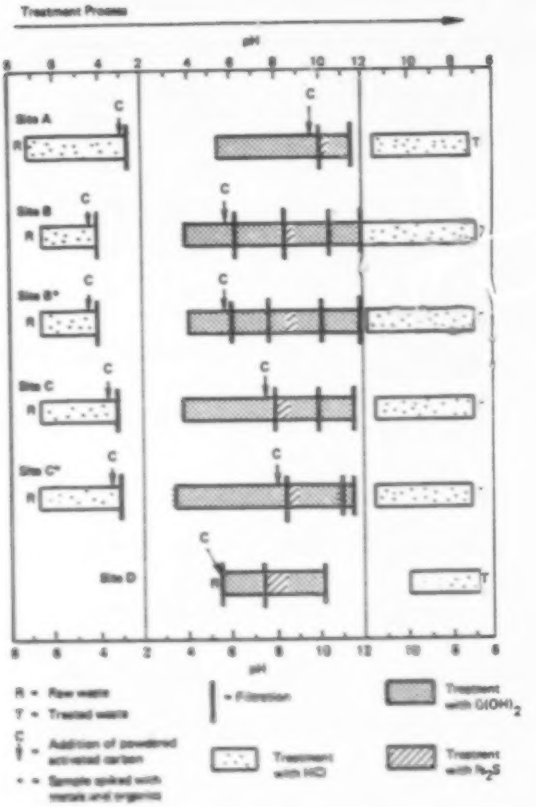


FIGURE 9 SUMMARY SCHEMATIC OF PILOT TREATMENT OF LEACIATES

TABLE 7. CHEMICAL USAGE ASSOCIATED WITH PILOT PLANT TREATMENT RUNS

Leachate Waste	$Ca(OH)_2$ (g/L)	Na_2S (g/L)	HCl (~37%) (ml/L)	Powdered Carbon (g/L)	Filter Aid (g/L)
Site A	0.453	0.059	1.47	5.7	1.7
Site B	4.60	0.52	0.87	5.7	6.6
Site B (spike)	4.90	0.49	16.8	5.6	9.4
Site C	1.78	0.26	2.33	5.2	5.4
Site C (spike)	2.21	0.27	4.67	5.3	5.6
Site D	0.430	0.058	0.29	10.7	7.2

to reduce effluent discharges. Such treatment generates sludges or solid residues that contain these metals in various chemical forms and concentrations. The objective of this program is to test processing techniques which mitigate the hazardous nature of these wastes. One such process is the separation of toxic metal precipitates from the waste via high gradient magnetic separation (HGMS).

TABLE 8. ESTIMATES OF SLUDGE VOLUME GENERATED DURING TREATMENT

Leachate from Site	Amount of precipitate formed in lab. tests (g/L)[a]	In pilot tests added: Powdered carbon (g/L)[a]	Filter aid (g/L)[a]	Sludge volume (cm^3/L) if sludge contains:[b] 50 wt. % water	75 wt. % water
A	0.38	5.7	1.7	13	28
B	3.52	5.7	6.6	25	57
C	1.08	5.2	5.4	19	42
D	1.25	10.7	7.2	31	70

a. Values are grams (dry weight) per liter of waste. Densities of these materials assumed to be: (1) precipitates, 2.2 g/cm^3; (2) powdered carbon, wet density of 1.6 g/cm^3; (3) filter aid, wet density of 1.5 g/cm^3.

b. Values are cm^3 of (wet) sludge generated per liter of raw waste.

HGMS is a filtration process which utilizes a filtering matrix of flux conducting material. Because of the geometry of the matrix, intense magnetic field gradients can be developed in the matrix which can capture weakly magnetic material. The HGMS process has been tested on a synthetic waste comprised of nickel hydroxide precipitation from a nitrate solution in a slurry of water and diatomaceous earth.

The preliminary data obtained from a pilot plant study indicate the HGMS can remove the nickel hydroxide, a weakly magnetic metal, although whether or not the performance of the filter is sufficient to make it a viable treatment process has not yet been determined.

REFERENCES

1. EPA. 1980. Electroplating Point Source Category Effluent Guidelines and Standards, Pretreatment Standards for Existing Sources. Federal Register, 44(130):45322-45328 (July 3, 1980).

2. EPA. 1980. Development Document for Effluent Limitations Guidelines and Standards for the Metal Finishing Point Source Category (Draft). EPA-440-1-80-091-A, U.S. Environmental Protection Agency, Washington, D.C.

3. Lyman, W.J. and G. Contos. 1980. Inorganic Hazardous Waste Treatment. In: Treatment of Hazardous Wastes, Proceedings of the Sixth Annual Research Symposium, EPA-600/9-80-011, U.S. Environmental Protection Agency, Cincinnati, Ohio. pp. 62-71.

4. NCWQ. 1975. Water Pollution Abatement Technology: Capabilities and Costs -- Metal Finishing Industry. National Commission on Water Quality, Washington, D.C.

TABLE 9. CONCENTRATION (mg/L) OF SELECTED HEAVY METALS IN PRE- AND POST-TREATMENT LEACHATE SAMPLES

	Site A[a]		Site B		Site C		Site D[c]	
Metal	Initial	Final	Initial[b]	Final	Initial[b]	Final	Initial	Final
Fe	27.5	1.1	741	3	53.4	3.0	322	<2
Mg	11.2	1.2	88.6	2.8	44.9	1.3	51.9	42[d]
Mn	5.54	0.02	4.91	0.27	2.59	0.27	85.1	4.2
Co	<0.05	<0.05	1.0 (<.05, <.1)	<0.1	1.2 (<.5, .3)	<0.1	<0.5	<0.5
Cr	0.016	0.008	8.01 (.028, <.02)	0.04	9.02 (<.08, <.02)	0.06	<0.08	<0.08
Cu	0.045	<0.005	8.34 (.094, .39)	1.15	8.86 (.09, .16)	0.60	0.14	<0.08
Ni	0.12	0.09	9.33 (<.01, <.03)	0.13	9.12 (<.1, <.03)	0.07	1.1	0.1
Pb	<0.05	<0.05	7.40 (<.05, <.2)	< 0.2	8.10 (<.5, <.2)	<0.20	<0.5	<0.5
Zn	0.072	0.049	10.0 (.16, .14)	< 0.05	9.65 (<.2, .35)	0.08	< 0.2	< 0.2
As	—[e]	—[e]	9.0 (-, .008)	0.033	6.5 (-, .003)	0.008	0.77	0.008

a. From laboratory tests.

b. Underlined values are artifically high due to addition of spikes in pilot runs; values in parentheses underneath are from unspiked laboratory and pilot plant runs, respectively. Where spike was added, "final" value is from the spike run.

c. From pilot plant run.

d. Questionable value; was <0.4 in final lab sample.

e. Not available.

EMERGING TECHNOLOGIES FOR THE DESTRUCTION OF HAZARDOUS WASTE
ULTRAVIOLET/OZONE DESTRUCTION

Barbara H. Edwards, John N. Paullin, Kathleen Coghlan-Jordan
Ebon Research Systems
Washington, D.C. 20011

ABSTRACT

Ebon Research Systems has investigated new technologies for the disposal of hazardous wastes. These methods are not state-of-the-art, but involve new technologies or a recent variation of an established technology. Information was acquired by computerized search, library searching, and personal contacts. A list of the emerging technologies includes: molten salt combustion, fluidized bed combustion, high energy electron bombardment, the catalyzed wet oxidation of toxic chemicals, dehalogenation of compounds by treatment with ultraviolet light and hydrogen, UV-chlorinolysis of organics in aqueous solution, the catalytic hydrogenation dechlorination of polychlorinated biphenyls, and Ultraviolet/Ozone destruction.

Ultraviolet/Ozone destruction (UV/Ozonation) is discussed in detail. Theory, specfic wastes treated, and economics are reviewed. Hazardous wastes are destroyed by treatment with a combination of UV light and ozonation. Wastes streams of up to 1% toxic contaminant can be treated. The blending of ozone's powerful oxidizing capacity with UV light's additional energy produces free radicals and excited-state species to accomplish the effective destruction of many hazardous organic chemicals. Among the wastes treated by UV/Ozonation are: PCBs, chlorodioxins such as TCDD, various hydrazines, nitrobenzene, and components of a copper process waste stream. Because ozone is a powerful oxidant, it cannot be shipped and must be generated on site. Waste stream effluent must be monitored for the possible generation of toxic intermediates during treatment.

Introduction

The quantity of hazardous wastes generated in the United States will exceed the capacity of landfills. The ultimate fate of many of these wastes in landfills is unknown. The argument can be espoused: Why inflict upon the next generation the waste disposal problems of this generation?

Conventional incineration has been a popular alternative to landfills, however there can be a problem with particulate emissions. Moreover, most municipal and industrial incinerators do not reach sufficiently high temperatures to completely destroy halogenated organics such as PCBs.

Ebon Research Systems has researched emerging technologies for hazardous waste disposal. These methods are not state-of-the-art, but involve a new technique. UV/Ozonation can effectively destroy toxic organics such as PCBs.

Ozone

Ozone (O_2) is a three atom allotrope of oxygen. It is second only to fluorine in electronegative potential and has long been recognized as a powerful disinfectant and oxidant of both organic and inorganic substances. Generated by solar energy, ozone is a natural ingredient of the earth's atmosphere. It is also generated by atmospheric oxygen with energy from lightning, and is associated with the operation of most electrical equipment. Under ambient conditions, ozone is a gas. Unreacted ozone decomposes in a matter of hours to simple, molecular oxygen. Low levels of ozone can damage delicate nasal, bronchial, and pulmonary membranes.

Mechanisms for UV/Ozonation Reactions with Organic Compounds

When ozone is used to oxidize organic compounds in aqueous solutions, gaseous phase ozone must dissolve in water in order to react with liquid phase organics. It has been reported that conditions favoring organic ozidation, alkaline pH, and elevated temperature also favor ozone decomposition. Elevated temperature reduces ozone solubility in water and causes inefficient ozone utilization even as organic oxidation increases. Ozone is relatively soluble in acid solution, but it decomposes rapidly with increasing alkalinity (Lee 4). However, temperature control is often uneconomical, and ozonation at high pH followed by neutralization will also increase costs.

In many cases, oxidation of organic different pH levels and varying temperatures with ozone alone results in the formation of highly refractory organic intermediates. If ozone treatment is combined with UV radiation, the UV activates the initial refractory compound and all subsequent species, permitting oxidation to carbon dioxide, water, and other elementary species (Prengle and Mauk 9).

The following groups are especially vulnerable to attack by ozone enhanced UV absorption:

- exposed halogen atoms
- unsaturated resonant carbon ring structures
- readily accessible multi-bonded carbon atoms
- alcohol and ether linkages

Shielded multi-bonded carbon atoms, sulfur, and phosphorous, are much less vulnerable.

There is a substantial difference in the chemistry involved and results achieved when the UV/Ozone process for treating hazardous waste is compared to straight ozonation. Ozonation of dilute solutions of organic species produces organic oxidation and hydroxyl radical formation. Bridging of carbon-carbon double bonds by ozone forms unstable ozonide intermediates that decompose into smaller oxidation species. This process continues until the ultimate final products, carbon dioxide and water or relatively stable refractory compounds (such as acetic acids or oxalic acids are formed (Prengle and Mauk 9).

When ultraviolet radiation, in the 180-400 nm range, is added to the process, 72-155 kcals/mole of additional energy is provided, and the O_3 molecule breaks down in oxidizing O species. This is ample energy for producing substantially more free radicals and excited state species for the initial compound and subsequent oxidation species than those produced by ozonation alone. As a result, excited atomic species (O), hydroxy (OH), and hydroperoxy (HO_2) radicals, and excited-state species (M), are produced from reactant molecules. These all greatly enhance the overall oxidation rate, prevent plateauing, and permit complete oxidation. The following is a simplified representation of how these excited species are probably formed:

$$O_3 + hv \longrightarrow O_2^* + O$$

$$O + H_2O \longrightarrow 2OH$$

$$O_3 + OH \longrightarrow HO_2 + O_2$$

$$M + hv \longrightarrow M^* \longrightarrow R, I + H$$

Overall:

$$\left.\begin{matrix} M \\ R \\ I \end{matrix}\right\} + OH,\ HO_2,\ O,\ O_2^* \longrightarrow$$

$$CO_2,\ H_2O,\ Cl^-,\ SO_4^{-2},\ PO_4^{-3}$$

where M is the pollutant species being oxidized, R is a free radical species, and I is an intermediate molecular species (Prengle and Mauk 9).

Elevated UV light also accelerates ozone decomposition, thus using UV excessively results in less favorable economics (Prengle et al. 8). However, no generalization regarding requirements can be made because of the wide variation in the reactivity of species. Free cyanide is oxidized by ozone without elevated temperature or UV, but iron-complexed cyanides have maximum practical limits for temperature and UV requirements. It is better to treat acetic acid at naturally occurring pH rather than neutralize, yet phenol destruction is not strongly pH dependent (Prengle et al. 8).

To summarize, the overall mechanism of UV/Ozone photo-oxidation of the pollutant species in aqueous solution occurs by a combination of the following:

- O_3 photolysis to produce oxidizing O species
- H_2O photolysis and reaction with O_3 to produce OH
- M photolysis to produce M^* and free radicals

The free radicals participate in a sequence of oxidation reactions leading to the final oxidation products. For M-species that are low UV absorbers, the rate controlling mechanism is photolysis oxygen species oxidation, but for high UV absorbers, M-species photolysis is rate controlling.

Mathematical models have been developed to determine the overall rate equation for the UV/Ozone process. A rate equation was proposed to describe the reaction in the intermediate stage. The rate during this period was described as a simple function of superficial gas velocity, ozone partial pressure, and the contaminant concentration. It was concluded, the destruction rate for toxic organic chemicals is directly proportional to the toxic organic chemical concentration and to the 1.5th power of the ozone feed rate. These models may provide a useful tool for design and scale-up of ozone contactors (Lee 4).

Ozone Generators

Unlike most chemicals, there is no controlled available natural source for ozone, and it is not practical to ship it or store it in containers. Consequently, ozone is generated on-site by the user. Ozone is generated when an oxygen molecule is sufficiently excited to disassociate into atomic oxygen; further collisions with oxygen molecules then cause the formation of the ozone molecule. Excitation energy can be supplied by ultraviolet light or high voltage (Klein et al. 3).

Oxygen is converted into ozone as follows:

$$3O_2 \longrightarrow 2O_3$$

Most ozone generators employ high voltage, and produce a corona discharge (also know as an silent arc discharge or brush discharge). The following conditions are necessary to produce a corona discharge:

- two electrodes separated by a gap
- a gas in the gap
- sufficient voltage potential between the two electrodes to cause current flow through the dielectric and gas (Ozone Research and Equipment Corporation 7)

The electrodes can be flat, tubular, or any configuration that allows the opposing surfaces to be parallel. The distance between the parallel surfaces of the electrodes should be large enough to ensure uniform current flow. A gap smaller than certain critical size may restrict air flow to a point of excessive pressure drop through the unit, while a large gap increases voltage requirements (Klein et al. 3).

The two basic types of commercial ozone generators in use are the concentric tube generator, and the parallel plate generator. The concentric tube system, first devised by Siemens, can be modified to operate at higher pressures than the plate design (Klein et al. 3). In a concentric tube generator, a glass electrode coated with a metal is surrounded by a second electrode that is a metal tube. In some designs, there is a stainless steel center electrode, with the glass dielectric tube concentric on the outside. The glass tube is coated with a metal that serves as the second electrode. Glass functions as a dielectric to increase the voltage gap between the electrodes without sparking. Ozone is formed from the oxygen in the gap between the tubes.

The more complex Otto system uses high voltage parallel plates that alternate with ones that are water cooled. Gas flows in the air gaps between the plates. There is more generating surface for a given volume with the parallel plate design when compared to the concentric tube design. Air cooling may replace water cooling, because water cooling is more costly.

Yet, many years of experience with water systems have developed relatively trouble free techniques (Klein, et al. 3).

Dielectric

The operational efficiency of an ozone generator is dependent on design and engineering considerations. The dielectric material selected should have both a high electrical resistance and high thermal conductivity. Since these properties rarely occur together in a material, the dielectric is usually chosen for its high electrical resistance, and used at a minimum thickness to overcome heat transfer deficiencies. Glass or other ceramic materials are usually used.

Pressure

The operating pressure should provide sufficient force to deliver ozonized gas to the contacting vessel. The pressure may have to overcome a back pressure of water at the reactor. As pressure affects the electrical impedance of the system, the operating pressure must be correlated with the air gap and preferred voltage (Klein et al. 3).

Flow Rate

The time that the feed gas is in the electrical discharge determines the concentration of ozone in the effluent. This concentration can vary from 0.5-10 wt% in a well designed, efficient generator operating at ideal conditions. Klein notes that the power efficiency drops rapidly as the ozone concentration increases.

Temperature

Approximately 90% of the energy applied to the ozonator is lost as heat. As the ozone decomposition rate increases with increasing temperature, provisions should be made for the rapid removal of excess heat. As ozone generator temperature increases, the dielectric material changes thermal characteristics and is subject to rupture. Because critical generator dielectric temperatures are relatively low (120°-130°C), the economics of refrigeration or coolant quantity supplied to the system must be evaluated versus the temperature of the ozone stream (Ozone Research and Equipment Corporation 7). Water is usually considered a more efficient medium for heat transfer than air. Water used for cooling ozonators need not be of high quality, and when it passes through the generator it is not degraded or changed.

Feed Gas

Ozone generation using oxygen is approximately twice as efficient as air (ozone generated from air requires at least twice the power of an equal amount of ozone generated from pure oxygen). However, the cost of pure oxygen is more than twice the cost of air. Unless oxygen is recovered via a closed system, it is cheaper, especially when ozonate is generated at less than 225 kg/day, to generate ozone from air. A recent development is a technique that uses a swing cycle to concentrate oxygen from air by alternate passage through molecular sieves (Derrick and Perrich 2).

Power

The major operating cost for ozone manufacturing is the cost of electric power. Of the total power utilized in ozone generation, approximately 10% is used to actually produce ozone. The remainder is consumed in air handling, air preparation, and waste heat. The use of higher frequencies increases ozone generation efficiency, yet the electrical cost of the high frequencies may offset the gain. This situation may be altered with new advances in solid state technology, according to Klein.

Destruct Systems

The reactor is a key element in the efficient utilization of ozone. The reactor should be designed for optimum ozone utilization, following established principles of mass transfer and reaction kinetics (Derrick and Perrich 2). In some cases, ozone not consumed in the primary reactor system can be reused or applied beneficially to another system. However, it may be necessary to provide a destruct system to guarantee removal of any unused ozone from the system before the gas stream is discharged to the atmosphere. There are three types of destruct systems: thermal, catalytic, and combination. Thermal systems heat the entire gas stream to a high temperature for a specific period of time (600°C for 1 second). Catalytic systems heat the gas to 250°C, and then pass the gas stream through a solid phase catalyst bed for ozone destruction. The catalysts are proprietary. Combination systems represent a trade-off between heating costs and catalyst costs. In all cases, heat recovery should be considered (Derrick and Perrich 2).

Hazardous wastes treated include PCBs, dioxins, hydrazines, nitrobenzene, and a copper process waste stream.

TCDD

2,3,7,8-tetrachlorodibenzo-p-dioxin was treated with an UV/Ozone system by researchers at California Analytical Laboratories and the Carborundum Company (Wong, et al. 11). Two types of ozonation systems were used: (1) purified oxygen to generate ozone. (2) a commercial unit was used. One ppb of TCDD was completely degraded. OCDD, a common dioxin impurity in the wood treatment agent PCP (pentachlorophenol) was also successfully degraded. These preliminary studies indicate the feasibity of UV/Ozone degradation systems for the treatment of dioxins in a waste stream (Wong et al. 11).

Hydrazine fuels

The hydrazine family of fuels includes hydrazine, monomethylhydrazine, and unsymmetrical hydrazine as well as mixtures of these compounds. A study for the United States Air Force investigated the effect of UV/Ozonation on these compounds. The following conclusions resulted:

- The presence of UV light in thee reactor reduces half-life valuess (t 1/2), and increases reaction rates for the ozonation of the hydrazine fuels over ozone reactions in the absence of UV light.
- An increase in solution pH, increases the oxidation rate of the hydrazine fuels.
- The quantity of methanol produced from ozone oxidation of monomethylhydrazine is proportional to the species concentration.
- Monomethylhydrazine decomposition during oxygen or air sparging is greatly enhanced by UV light.
- Increasing ozone partial pressure decreased half-life values, but ozone utilization efficiency is reduced.
- An increase in species concentration produced an increase in the required retention time to achieve the proper effluent levels (Sierka and Cowen 10).

Nitrobenzene

Investigators at the Westgate Research Corporation studied the effects of ozone and UV/Ozonation on nitrobenzene. The authors concluded that the UV/Ozonation of organic compounds in water at levels of about 0.8 mM is probably not a free radical phenomenon. The intermediates oxalic and formic acids, although stable in the absence of UV light, were readily oxidized to carbon dioxide by the UV/Ozone system. (Leitis, et al. 5).

Copper process waste stream

A copper process waste stream containing primarily sodium sulfate, formic acid, an anionic surfactant, and EDTA was treated with UV/Ozonation by scientists at the Systems Products Division of IBM. In order to discharge the treated effluent into the plant clarification system, the final concentration of EDTA was limited to 5 ppm (Macur, et al. 6). The following conclusions were reached:

- Waste solution pH should be maintained in the 4-6 range.
- Iron (III) levels should be below 5 ppm.
- Copper (II) levels should be less than 1 ppm.

PCBs

A pilot plant was set up at a General Electric Company plant to demonstrate the efficiency and cost-effectiveness of a commercial ULTROX UV/Ozone system to destroy PCBs. PCB levels in the range of 5-40 ppm were studied. Many of the runs had no PCB residue in the effluent.

An economic projection for a 150,000 gallons per day ULTROX treatment plant designed to attain 1 ppm or lower PCB in the effluent (assuming a 50 ppm feed) varied from $300,000-$350,000. Design and economic data for a 40,000 gallons per day (151,400 liters per day) plant are summarized below in Tables 1 and 2 (Arisman and Musick 1).

TABLE 1. DESIGN DATA FOR A 40,000 GPD (151,400 LITERS/DAY) ULTROX PLANT

Reactor	
Dimensions,	
Meters (LxWxH)	2.5 x 4.9 x 1.5
Wet Volume, Liters	14,951
UV Lamps	
Number of 65 watt lamps	378
Total Power, KW	25
Ozone Generator	
Dimensions,	
Meters (LxWxH)	1.7 x 1.8 x 1.2
gms Ozone/minute	5.3
kg Ozone/day	7.7
Total Power, KW	7.0
Total Energy required (KWH/day)	768

TABLE 2. EQUIPMENT PLUS OPERATING AND MAINTENANCE COSTS 40,000 GPD ULTROX PLANT

Reactor	$94,500
Generator	30,000
	$124,500
O & M Costs/Day	
Ozone generator power	$4.25
UV lamp power	15.00
Maintenance (Lamp Replacement)	27.00
Equipment Amortization (10 years @ 10%)	41.90
Monitoring labor	85.71
TOTAL/DAY	$173.86
Cost per 1,000 gals (3,785 liters) with monitoring labor	$4.35
Cost per 1,000 gals without monitoring labor	$2.20

Source: Arisman and Musick, General Electric Co., Hudson Falls, NY, Zeff and Crase Westgate Research Corp., West L.A., Calif.

Advantages of UV/Ozonation

- Aqueous or gaseous waste streams can be treated.
- Capital and operating costs are not excessive as compared to incineration.
- The system is readily adaptable to the on-site treatment of the hazardous waste.
- UV/Ozonation can be used as a final treatment for certain wastes.
- It can be used as a preliminary treatment for certain wastes.
- Effluent discharge standards can be met.
- Modern systems are usually automated, thereby reducing labor requirements.

Disadvantages of UV/Ozonation

- Ozone is a non-selective oxidant; the waste stream should contain primarily the waste of interest.
- Certain compounds because of their structure are not amenable to UV/Ozonation (high refractory index).
- UV/Ozone systems are generally restricted to 1% or lower levels of toxic compounds. The system is not amenable to bulky wastes.
- Toxic intermediates may persist in the waste stream effluent.
- Ozone decomposed rapidly with increasing temperature. Excess heat must be removed rapidly.

Conclusions

UV/Ozonation is a viable emerging technology for the treatment of hazardous wastes when compared to the problems of landfills and conventional incineration. UV/Ozonation is not cost-prohibitive from the standpoint of capital plus operating and maintenance costs (O & M). The process is particularly suitable for the on-site treatment of hazardous wastes.

REFERENCES*

1. Arisman, R.K. and R.C. Musick. 1980. Experience in operation of a UV-Ozone ULTROX pilot plant for destroying PCBs in industrial waste effluent. Presented at the 35th Annual Purdue Industrial Waste Conference, May, 1980.

2. Derrick, D.K. and J.R. Perrich. 1979. Guide to ozone equipment selection. Pollution Engineering, 11:42-44.

3. Klein, M.J. et al. 1973. Generation of ozone. Presented before the First International Symposium on Ozone for Water and Wastewater Treatment.

4. Lee, M.K. 1980. Study of UV-ozone reaction with organic compounds in water. Presented before the Division of Environmental Chemistry, American Chemical Society, Houston, Texas.

5. Leitis, E. et al. 1979. An investigation into the chemistry of the UV/Ozone purification process. Presented at the 4th World Ozone Congress, Houston, Texas.

6. Macur, G.J. et al. 1980. Oxidation of organic compounds in concentrated industrial waste water with ozone and ultraviolet light. Presented at the 35th Annual Purdue Industrial Waste Conference, Layfayette, Indiana.

7. Ozone Research and Equipment Corporation, Phoenix, Arizona. Ozone Technology. Brochure 124.

8. Prengle, H.W. et al. 1975. Ozone/UV process effective wastewater treatment. Environmental Management, 54:82-87.

9. Prengle, H.W. and C.E. Mauk. 1978. New technology: ozone/UV chemical oxidation wastewater process for metal complexes, organic species and disinfection. The American Institute of Chemical Engineers Symposium Series, 74:228-243.

10. Sierka, R.A. and W.F. Cowen. 1980. The catalytic ozone oxidation of aqueous solutions of hydrazine, monomethylhydrazine, and unsymmetrical dimethylhydrazine. Presented at the 35th Annual Purdue Industrial Waste Treatment Conference, Layafette, Ind.

11. Wong, A.S. et al. 1979. Ozonation 2,3,7,8-tetrachlorodibenzo-p-dioxin. Presented at the Symposium on the Chemistry of Chlorinated Dibenzodioxins and Dibenzofurans, American Chemical Society National Meeting, Washington, D.C.

---

* ULTROX is a registered trademark.

EVALUATION OF CATALYZED WET OXIDATION FOR TREATING HAZARDOUS WASTE

Richard A. Miller
Robert D. Fox
David M. Pitts

IT Enviroscience
Knoxville, Tennessee 37923

ABSTRACT

This paper describes the evaluation of a unique, patented catalyst system for treating toxic and hazardous waste from active and abandoned chemical landfills. The catalyst system uses an acidic solution of bromide, nitrate, and manganese ions to destroy organic residues and aqueous wastes. Fifteen compounds were selected to represent the wide variety of wastes which could be found in a chemical landfill. Batch oxidations of these compounds were performed in a 1-liter stirred autoclave to determine the destruction rate and by-products of the process. While detailed analysis of the results has not been completed, sufficient data are available to provide insight into effectiveness and applicability of the process. Preliminary designs of treatment processes have been made based on the demonstrated destruction rates. Cost estimates for these processes are provided to permit assessment of the technology for treating hazardous wastes.

INTRODUCTION

The program described in this paper had as its goal the application of a new and novel catalytic wet oxidation technology for the treatment of toxic and hazardous waste materials. On the basis of preliminary range-finding testing and economic evaluation, the technology appears to have wide ranging applicability and potential for alleviating significant waste disposal problems facing the United States. Candidate wastes which are potentially treatable by this technology include aqueous wastes, organic liquids, sludges, and solids. Of particular interest to this project is the development and application of new technology to the problems associated with abandoned chemical waste disposal sites. The Love Canal and the Valley of the Drums are two among many already unearthed. The estimate of the number of such sites in the United States and the cost to clean them up is staggering. Typical of the disposal problems of these sites are treatment of leachate and groundwater around the site and the ultimate disposal of the sludges, soils, liquids, solids, and containers on the site.

The most desirable technology for dealing with the problem of chemical disposal sites would be a process that will 1) achieve complete destruction of toxic and hazardous chemicals and minimize the by-products and chemical remnants requiring disposal; 2) minimize the energy required for disposal, especially supplemental fuels; 3) have low chemical usage; 4) have few unit operations;

5) have low volume effluents, such that polishing treatment to achieve total containment can be readily implemented; 6) be easily pilot planted; and 7) be transportable to the landfill sites.

Incineration systems are generally regarded as capable of meeting the first objective, but run into difficulty in the other areas. Conventional wet oxidation systems have the capability to meet the last six criteria, but are limited in the first. Other destructive processes such as biological treatment or chemical oxidation are either ineffective or very expensive. IT Enviroscience believes that the unique features of its catalyzed wet oxidation process provide the potential to overcome the shortcomings of other destruction processes. It approaches the omnivorous and total destruction characteristics of incineration while retaining the advantages of wet oxidation systems in other areas.

CATALYZED WET OXIDATION PROCESS CONCEPT

The catalyzed wet oxidation process is based on U.S. Patent 3,984,311, originally assigned to The Dow Chemical Company and now assigned to IT Enviroscience for development and commercialization. The patent teaches the use of a co-catalyst system consisting of bromide and nitrate anions in an acidic, aqueous solution. Continued research with the co-catalyst system has led to the development of a new catalyst mixture which is more effective for oxidizing insoluble organics. The new catalyst system consists of bromide, nitrate, and manganese ions in acidic solution. A patent for the new catalyst has been allowed and assigned to IT Enviroscience. The destruction of most organics by these catalyst systems is rapid and essentially complete.

The keys to the operation of this catalyst system are the mechanism of oxygen fixation and the fact that it is a water-soluble, single-phase catalyst system--a homogeneous catalyst as contrasted to a heterogeneous catalyst. In conventional wet oxidation, heat and pressure are used to drive the dissolution of oxygen from air and the reaction with dissolved organics in aqueous solution. In the bromide-nitrate-manganese catalyst system the transfer of oxygen to the dissolved state is speeded up by using very rapid gas and liquid reactions associated with the catalyst components. The importance of the enhanced oxygen transfer is the ability to oxidize organics at much lower temperatures than uncatalyzed wet oxidation, 165—200°C versus 250—325°C. The lower operating temperatures also mean lower operating pressures which not only reduces capital cost but operational problems.

The second important aspect of the catalyst system is its homogeneous nature which permits application to the destruction of toxic or hazardous organic residues, such as still bottoms or other organic wastes. The advantages of a homogeneous catalyst are best utilized by using a reactor design which is different from conventional wet oxidation processes. In simplest form the reactor, a continuously stirred tank reactor (CSTR) contains the catalyst solution. Air and the waste are continuously pumped into the reactor and the organics are oxidized with the heat of reaction driving off water. The only materials to leave the reactor are CO_2, N_2, water vapor, any volatile organics and inorganic solids formed. Water is condensed and returned to the reactor, if necessary, as are condensable organics. Any inorganic salts or acids which may be formed have to be removed by treatment of a close loop stream of catalyst solution. Such treatment is individually designed utilizing conventional technologies, such as filtration or distillation. The vent gases from the reactor are low in volume and may, if necessary, be treated by conventional techniques, such as absorption, adsorption, or scrubbing. The most important features of this process concept are that nonvolatile organics remain in the reactor until destroyed, and that there is no aqueous bottoms product.

EXPERIMENTAL

Compound Selection

The study of a process associated with chemical wastes needs to evaluate a wide range of chemical compounds to evaluate the applicability of the process. In order to meet this requirement fifteen compounds were selected from various chemical groupings of the EPA priority pollutant list. The specific compounds chosen from each grouping were made based on the likelihood of finding the chemical in industrial waste and chemical disposal sites. In certain cases a lower toxicity compound was substituted for a highly toxic compound, e.g., diphenylhydrazine substituted for benzidine, when it presented an unacceptably high risk to laboratory personnel. The chemical groupings and the compounds studied were:

- Halogenated hydrocarbons
    - Ethylene dibromide
    - Hexachlorobutadiene
    - Trichloropropane
- Pesticides
    - Atrazine
    - DDT
    - Malathion
    - Mirex
- Phenols
    - Pentachlorophenol
- Phthalates
    - Di-n-butyl phthalate
- Polynuclear aromatics
    - Chloroanthracene
- Miscellaneous
    - Acetonitrile
    - Chloroaniline
    - Diphenyl hydrazine
    - Nitrobenzene
    - o-Xylene

Experimental Method

The experimental evaluation of catalyzed wet oxidation was conducted in a 1-liter agitated titanium autoclave. The destruction rate of the compounds was measured at various operating conditions with batch reactions. Typical operating conditions were 165—250°C, 0.5% Br, 5.0% NO_3, 0.25% Mn, 30—120 minutes reaction time, and 20% excess oxygen over stoichiometric. The procedure for conducting the oxidation reactions consisted of loading the reactor with the desired quantity of deionized water, HBr, and the organic to be oxidized. The reactor was sealed, purged with oxygen, and pressurized with sufficient oxygen to totally oxidize the organic. The reactor was then heated to the desired operating temperature and the remaining catalysts, HNO_3 and $MnSO_4$, were added to the reactor with oxygen pressure. The reaction was run for the desired time period. At the termination of the reaction, the reactor was cooled to room temperature with cooling water. The pressure was then vented and any free bromine was reduced to bromide by the addition of 10 ml of sodium bisulfite solution to prevent operator exposure to toxic bromine vapors. The reactor was opened and the aqueous contents were aspirated from the reactor. All internal surfaces of the reactor were rinsed twice with solvent, methylene chloride. The solvent rinsings were aspirated from the reactor and combined with the aqueous effluent. The aqueous phase was extracted with the solvent rinse and two successive 50-ml portions of solvent to recover unreacted organics and reaction by-products. The combined solvent extracts were analyzed by gas chromatography and gas chromatography/mass spectrometry (GC/MS). The destruction rate of the organic was also measured by the formation of CO_2, by gas chromatography, and the formation of Cl^- (from chlorinated organics), by ion chromatography.

These measurements were used to determine the completeness of the organic destruction.

Experimental Results

The compilation and interpretation of the experimental results has not been completed at this time. Initial examination of the data reveals that catalyzed wet oxidation was effective in destroying most of the compounds tested. The oxidation of atrazine, butyl phthalate, chloroaniline, diphenyl hydrazine, ethylene dibromide, malathion, pentachlorophenol and xylene was rapid (<60 minutes) and essentially complete (>60% destruction to CO_2) under mild oxidation conditions (165—200°C). Some of the compounds, acetonitrile, chloroanthracene, DDT, hexachlorobutadiene, nitrobenzene and trichloropropane required higher oxidation temperatures (200——250°C), longer reaction times (up to 120 minutes), and were only partially oxidized to CO_2 (<40% destruction to CO_2). Mirex was the most resistant to oxidation by the catalyst system with <10% destruction even at very high temperatures, 275°C. While these results are very general, the ability of the bromide-nitrate-manganese catalyst system to destroy a wide range of organics was demonstrated.

PROCESS DESIGN AND ECONOMICS

In applying this technology to destroying the contents of a chemical landfill a "worst case" approach was used to design a treatment process and estimate the operating costs. This general basis approach should be used because the contents of a landfill will be an unknown mixture of organics and it is safest to assume a slow destruction rate for the mixture. Two different processes were designed to provide the basis of estimating destruction costs. The equipment basis for both processes is a 1000-gallon reactor system which can be transported to the landfill site. The first process is designed to continuously oxidize organic residues with moderate-slow destruction rates. Under continuous feed conditions, organic residues are added to the reactor at a rate that represents the steady-state destruction rate and the organics are consumed at the rate they are added; a constant "heel" of organics is maintained in the reactor. At some point, when the catalyst solution may need to be disposed of, the reactor is batch-operated to destroy the heel of organics remaining in the reactor. It is at this point that total destruction of the organics is achieved and concentrations are reduced to ppm or ppb levels. It is estimated that the operating, (without equipment depreciation) cost for destroying organic residues with catalyzed wet oxidation will be 15 to 30 cents per pound of organic.

The second process is designed to treat an aqueous waste with 4% organic. This process differs from the first in the quantity of water that must be handled. The process handles the additional water by utilizing the heat of reaction of the organics to drive the water overhead for removal with a condenser. For dilute aqueous wastes, where insufficient energy is released by the oxidation of the organics to evaporate all of the incoming and formed water, it is necessary to provide an evaporator to maintain the catalyst concentration in the reactor. Energy for the evaporation of the dilute catalyst solution in the reactor comes from the reactor vent gas. The operating cost for this process, less depreciation of equipment, is estimated to be 27 cents per gallon of aqueous waste.

CONCLUSIONS

The catalyzed wet oxidation process has successfully destroyed a wide range of organics in laboratory batch tests. The strong oxidizing power of the homogeneous catalyst system coupled with a process design which retains unreacted organics makes this process a viable technology for solving the problems associated with chemical disposal sites. Other aspects of the catalyzed wet oxidation process such as energy efficiency, low chemical usage, low volume effluents, and portability also make the process attractive for solving industrial waste problems.

This research was funded by U.S. Environmental Protection Agency Contract No. 68-03-2568, Work Directive T-7016.

REGISTRATION REQUIREMENTS FOR PESTICIDE LABELING - LAND DISPOSAL

Dimitrios Kollias and Janet Brambley
Systems Research Company
Philadelphia, PA 19104

ABSTRACT

An outline is presented of the information necessary to initiate the development of data requirements and testing protocols to evaluate label statements on the land disposal of pesticides, in compliance with the proposed guidelines for registering pesticides in the United States, 40-CFR-162. The information surveyed includes soil studies, physicochemical degradation (hydrolysis and photolysis) of pesticides, soil-pesticide interactions (adsorption, volatility and leaching), metabolism (soil-microorganism relationships, aerobic and anaerobic metabolism), effects on highter plants and animals, which apply to land disposal methods. The lack of studies carried out with pesticides in amounts compatible with the actual disposal levels, as opposed to use levels, is evident, as in the absence of data on pesticide mixtures, pesticide interactions, etc.

INTRODUCTION

Pesticide containers are required by law to carry on the label instructions for the disposal and storage of excess pesticides and pesticide containers. The intelligibility and reliability of these statements has been questioned in the past (1).

The USEPA under 40-CFR-162 has proposed guidelines for registering pesticides in the United States, specifying the data required to support the registration of a product, describing the standards for acceptable testing, providing references to test protocols in the literature, and outlining the format for data reporting. Under CFR Section 162-62-13, environmental chemistry data are required to support pesticide label statements on disposal and storage of registered manufactured use products and all formulated products.

The object of this contract is to generate data requirements and testing protocols for better evaluation of specific pesticide disposal and storage recommendations, with special emphasis on the development of improved label directions for proper storage and disposal of excess pesticides and pesticide containers.

The chemical characteristics of pesticides and their diversity of use may preclude the development of universally acceptable environmental chemistry data requirements. Nevertheless, the scope of work requires the development, as nearly as possible, of universally acceptable testing protocols to support label statements on pesticide disposal and storage.

A recent survey (2) of manufacturers' labels revealed that land disposal was the most frequently recommended method for the disposal of excess pesticides.

Several other studies (3-6) concluded that land disposal could conceivably be an effective method for the disposal of at least some of the individual pesticides currently in use. Actual evidence in this respect, especially field studies, is scarce or non-existent.

DATA REQUIREMENTS AND TESTING

General

Land disposal of waste pesticides encompasses all methods by which waste is deposited in or on land, including burial, soil injection, soil mounds, soil pits, infiltration/evaporation basins, soil in corporation, etc. The waste pesticides that might be disposed in this manner are primarily those generated in agricultural operations, including obsolete and expired pesticides, unused spray mixes, rinses, etc. Practically all research has been conducted with use strengths and dilute solutions of pesticides. The effectiveness of each method depends on the nature and amount of pesticide disposed and the soil and environmental conditions prevailing at the disposal site.

The tests proposed below must be conducted for all land disposal methods, regardless of their nature, although specific methods might require additional tests which are not outlined herein. Since the disposal of pesticides in the soil has features in common with their actual use, some of the testing requirements will duplicate those for use, found in 40 CFR Subpart D, Environmental Chemistry, 163.62-1 to 163.62-11.

Soil Studies

Studies of the physical properties of the soil (7-11) must be conducted to determine relative particle size, clay, silt, sand, mineral and organic composition, salinity, and acidity, all of which affect the absorption and adsorption characteristics and the permeability of the soil to pesticides. The geology of the area must be investigated to determine the location of groundwater and the presence and position of impervious strata. A topographical survey may also be required to determine surface features, flood and erosion potential, and the operation of wells and other structures. Soils to be tested must include the specific soil of the disposal site, if known, soils typical of the area where the pesticide is to be disposed, or a standard soil sample of known properties.

Physico-chemical Degradation

Pesticide molecules are altered in the soil by physical and chemical processes. The amount of degradation of pesticides by hydrolytic (12-13) and photolytic (14-18) processes must be determined, and the decomposition products identified. Studies must include the concentrated pesticide.

Soil-Pesticide Interactions

Small scale studies must be conducted to determine the effect of the soil on the pesticide. The physical composition of the soil and the physical properties of the pesticide will determine the adsorption (19-25),volatilization (26-29), leaching (12,23,30-32) and water dispersal of the pesticide, which, in turn, determine the mobility of the pesticide in soil. Even pesticides of the same chemical family have widely different soil retention characteristics. These factors will also be affected by the climatic characteristics of the area, so that the tests should be conducted at as close to natural environmental conditions prevailing at the time of disposal as possible. Tests will be conducted with the commercial pesticide formulations, use strength and dilute solutions.

Metabolism

When a pesticide is applied to a soil, it immediately has an effect on the living organisms of the soil and may be affected by them. Accordingly, determination of the effects of the microorganisms on pesticides is essential (33-38). The pesticide may be available for metabolism under aerobic or anaerobic conditions, and it may have an effect on the microbial population of the soil (31,49-53). Pesticides such as fungicides and nematicides are aimed at soil populations; the effect on nontarget organisms must be determined (37,54-62).

Effects on Higher Plants and Animals

The effects of the pesticide on the higher plants and animals living in the disposal area, or that could be expected to come into contact with the pesticide must be determined. The effects of herbicides on plant life and of insecticides on insects are known, but each class of pesticides has the potential for affecting nontarget organisms. These organisms will include plants, amphibians, birds and mammals.

The tests must include investigations of accumulation and acute and chronic toxicity and, for mammals, investigations of the possible mutagenicity, teratogenicity and carcinogenicity. All these tests are given in 40 CFR 163.70-1 to 163.72-6.

DISCUSSION

A reasonable evaluation of the effectiveness of pesticide disposal can be made on the basis of the following criteria: no leaching of pesticide into ground or surface waters; absence of air pollution due to the volatilization of pesticide; destruction of more than 99.999% of the pesticide within the useful life of the disposal site; lack of long-term alterations in the populations of microorganisms and higher organisms living on or near the site; rate of pesticide leaching held at less than 0.1 ft/year; and site location away from an environmentally sensitive area.

Evaluation of pesticide detoxification, however, is hampered by the fact that the available information is overwhelmingly based on research performed with use strength and dilute solutions of pesticides. Furthermore, since the optimum degradation conditions for pesticides in soils are largely unknown, more research is required to determine the loading rates and lifetime of a given disposal site.

Moverover, disposal research has been concentrated on single, pure compounds. Accordingly, the land disposal of pesticide mixtures, as well as the effect of solvents, two conditions currently encountered in actual practice, are in need of exhaustive scrutiny.

There is a definite lack of information regarding the detoxification mechanisms and ultimate fate of pesticides in the soil, volatility, leaching, migration and residual toxicity of pesticides at disposal rather than use levels. The tests and data requirements outlined above are based primarily on studies carried out with pesticides in use strength, or 1-10 lb/acre. Accordingly, it is only reasonable to assume that the results yielded by disposal levels, which can be as high as 10,000 lb/acre, or even more, may vary to different degrees.

REFERENCES

1. Klee, A.K. 1980. Current Research on Hazardous Waste Assessment and Control. In: Treatment of Hazardous Waste. Proceedings of the Sixth Annual Research Symposium, D. Schultz ed. EPA-600/9-80-011, U.S. Environmental Protection Agency, Cincinnati, OH. pp. 1-7.

2. Brambley, J., and D. Kollias. 1980. In: Treatment of Hazardous Waste. Proceedings of the Sixth Annual Research Symposium, D. Schultz ed. EPA-600/9-80-011, U.S. Environmental Protection Agency, Cincinnati, OH. pp. 101-111.

3. Lawless, E.W., T.L. Ferguson, and A. F. Meiners. 1975. Guidelines for the Disposal of Small Quantities of Pesticides. EPA-670/2-75-057, U.S. Environmental Protection Agency, Cincinnati, OH. 331 pp.

4. Sanborn, J.R., B.M. Francis, and R. L. Metcalf. 1977. The Degradation of Selected Pesticides in Soil: A Review of the Published Literature. EPA-600/9-77-022, U.S. Environmental Protection Agency, Cincinnati, OH. 617 pp.

5. Marsh, J.R., H.-T. Phung, and D.E. Ross. 1978. Disposal of Dilute Pesticide Solutions. SCS Engineers, Long Beach, CA. Contract No. 68-01-4729, U.S. Environmental Protection Agency, Washington, D.C. 109 pp.

6. Shih, C.C., and D.F. Dal Porto. 1975. Handbook for Pesticide Disposal by Common Chemical Methods. Final Report, EPA-530/SW-112C, U.S. Environmental Protection Agency, Washington, D.C. 109 pp.

7. Allison, L.E. 1975. Organic Carbon. In: Methods of Soil Analysis, C.A. Black, D.D. Evans, J.L. White, L.E. Ensminger, and F.E. Clark (eds). Amer. Soc. Agron. Publ. No. 9. Madison, WI. pp. 1367-1378.

8. Broadbent, F.E. 1965. Organic Matter. In: op. cit. pp. 1397-1400.

9. Chapman, H.D. 1965. Cation-Exchange Capacity. In: op. cit. pp. 891-901.

10. Day, P.R. 1965. Particle Fractionation and Particle-Size Analysis. In:

op cit. pp. 545-567.

11. Peech, M. 1965. Hydrogen-Ion Activity. In: op. cit. pp. 914-926.

12. Krzeminski, S.F., C.K. Brackett, and J.D. Fisher. 1975. Fate of Microbial 3-Isothiazolone Compounds in the Environment: Modes and Rates of Dissipation. J. Agr. Food Chem. 23:1060-1068.

13. Gomaa, H.M., I.H. Suffet, and S.D. Faust. 1969. Kinetics of Hydrolysis of Diazinon and Diazoxon. Residue Rev. 29:171-180.

14. Koshy, K.T., A.R. Friedman, A.L. VanDerSlik, and D.R. Graber. 1975. Photolysis of Benzoic Acid 2-(2,4,6-Trichlorophenyl)-hydrazide. J. Agr. Food Chem. 23:1084-1088.

15. Nakagawa, M., and D.G. Crosby. 1974. Photodecomposition of Nitrofen. J. Agr. Food Chem. 22:849-853.

16. Nilles, G.P., and M.J. Zabik. 1975. Photochemistry of Bioactive Compounds. Multiphase Photodegradation and Mass Spectral Analysis of Basagran. J. Agr. Food Chem. 23:410-415.

17. Newsom, H.C., and W.G. Woods. 1973. Photolysis of the Herbicide Dinitramine (N^3,N^3-Diethyl-2,4-dinitro-6-trifluoromethyl-m-phenylenediamine). J. Agr. Food Chem. 21:598-601.

18. Su, G.C.C., and M.J. Zabik. 1972. Photochemistry of Bioactive Compounds. Photolysis of Arylamidine Derivatives in Water. J. Agr. Food Chem. 20:320-325.

19. Aharonson, N., and U. Kafkafi. 1975. Adsorption, Mobility and Persistence of Thiabendazole and Methyl 2-Benzimidazolecarbamate in Soils. J. Agr. Food Chem. 23:720-724.

20. Dao, T.H., and T.L. Lavy. 1975. Extraction of Soil Solution Using a Simple Centrifugation Method for Pesticide Adsorption-Desorption Studies. Soil Sci. Soc. Am. Proc. 42:375-377.

21. Harvey, R.G. 1974. Soil Adsorption and Volatility of Dinitroaniline Herbicides. Weed Sci. 22:120-124.

22. Murray, D.S., P.W. Santelmann and J.M. Davidson. 1975. Comparative Adsorption, Desorption, and Mobility of Dipropetryn and Prometryn in Soil. J. Food Agr. Chem. 23:578-582.

23. Rao, P.C.S., and J.M. Davidson. 1979. Adsorption and Movement of Selected Pesticides at High Concentrations in Soils. Water Res. 13:375-380.

24. Saltzman, S., L. Kliger and B. Yaron. 1972. Adsorption Desorption of Parathion as Affected by Soil Organic Matter. J. Agr. Food Chem. 20:1224-1226.

25. Wu, C.H., N. Buehring, J.M. Davidson, and P.W. Santelmann. 1975. Napropamide Adsorption, Desorption, and Movement in Soils. Weed Sci. 23:454-457.

26. Harper, L.A., A.W. White, Jr., R.R. Bruce, A.W. Thomas, and R.A. Leonard. 1976. Soil and Microclimate Effects on Trifluralin Volatilization. J. Environ. Qual. 5:236-242.

27. Jackson, M.D., and R.G. Lewis. 1978. Volatilization of Two Methyl Parathion Formulations from Treated Fields. Bull. Environ. Cont. Tox. 20:793-796.

28. Parmele, J.H., E.R. Lemon, and A.W. Taylor. 1972. Micrometeorological Measurement of Pesticide Vapor Flux from Bare Soil and Corn under Field Conditions. Water, Air, and Soil Pollut. 1:433-451.

29. Soderquist, C.J., D.G. Crosby, K.W. Moilanen, and J.E. Woodrow. 1975. Occurrence of Trifluralin and Its Photoproducts in Air. J. Agr. Food Chem. 23:304-309.

30. Helling, C.S. 1971. Pesticide Mobility in Soils I. Parameters of Soil Thin-Layer Chromatography. Soil Sci. Soc. Amer. Proc. 35:732-737.

31. Lichtenstein, E.P., T.T. Liang, and T.W. Fuhremann. 1978. A Compart-

mentalized Microcosm for Studying the Fate of Chemicals in the Environment. J. Agr. Food Chem. 26:948-953.

32. Lichtenstein, E.P., K.P. Schultz, and T.W. Fuhremann. 1972. Movement and Fate of Dyfonate in Soils under Leaching and Nonleaching Conditions. J. Agr. Food Chem. 20:831-838.

33. Benezet, H.J., and F. Matsumura. 1974. Factors Influencing the Metabolism of Mexacarbate by Microorganisms. J. Agr. Food Chem. 22:427-430.

34. Furukawa, K., and F. Matsumura. 1976. Microbial Metabolism of Polychlorinated Biphenyls. Studies on the Relative Degradability of Polychlorinated Biphenyl Components by Alkaligenes sp. J. Agr. Food Chem. 24:251-256.

35. Ou, L.-T., D.F. Rothwell, W.B. Wheeler, and J.M. Davidson. 1978. The Effect of High 2,4-D Concentrations on Degradation and Carbon Dioxide Evolution in Soils. J. Environ. Qual. 7:241-246.

36. Sikka, H.C., and J. Saxena. 1973. Metabolism of Endothall by Aquatic Organisms. J. Agr. Food Chem. 21:402-406.

37. Stojanovic, B.J., M.V. Kennedy, and F.L. Shuman, Jr. 1972. Edaphic Aspects of the Disposal of Unused Pesticide Wastes and Pesticide Containers. J. Environ. Qual. 1:54-62.

38. Van Alfen, N.K., and T. Kosuge. 1974. Microbial Metabolism of the Fungicide 2,6-Dichloro-4-nitroaniline. J. Agr. Food Chem. 22:221-224.

39. Bartha, R., and D. Pramer. 1965. Features of Flask and Method for Measuring the Persistence and Biological Effects of Pesticides in Soil. Soil Sci. 100:68-70.

40. Betts, P.M., C.W. Griddings, and J.R. Fleeker. 1976. Degradation of 4-Aminopyridine in Soil. J. Agr. Food Chem. 24:571-574.

41. Fleeker, J.R., H.M. Lacy, I.R. Schultz and E.C. Houkom. 1974. Persistence and Metabolism of Thiophanate-methyl in Soil. J. Agr. Food Chem. 23:592-595.

42. Gingerich, L.L., and R.L. Zimdahl. 1976. Soil Persistence of Isopropalin and Oryzalin. Weed Sci. 24:431-434.

43. Gowda, J.K.S., and N. Sethunathan. 1976. Persistence of Endrin in Indian Rice Soils under Flooded Conditions. J. Agr. Food Chem. 24:750-753.

44. Kazano, J., P.C. Kearney, and D.D. Kaufman. 1972. Metabolism of Methylcarbamate Insecticides in Soils. J. Agr. Food Chem. 20:975-979.

45. Marvel, J.T., B.B. Brightwell, J.M. Malik, M.L. Sutherland, and M.L. Rueppel. 1978. A Simple Apparatus and Quantitative Method for Determining the Persistence of Pesticides in Soils. J. Agr. Food Chem. 26:1116-1120.

46. Messersmith, C.G., O.C. Burnside, and T.L. Lavy. 1971. Biological and Nonbiological Dissipation of Trifluralin from Soil. Weed Sci. 19:285-290.

47. Parr, F.F., and S. Smith. 1969. A Multipurpose Manifold Assembly: Use in Evaluating Microbiological Effects of Pesticides. Soil Sci. 107:271-276.

48. Parr, J.F., and S. Smith. 1973. Degradation of Trifluralin under Laboatory Conditions and Soil Anaerobiosis. Soil Sci. 115:55-63.

49. Schooley, D.A., K.N. Cresswell, L.E. Starger, and G.B. Quislad. 1975. Environmental Degradation of the Insect Growth Regulator Isopropyl (2E, 4-E)-11-methoxy-3,7,11-trimethyl-2,4-dodecadienoate (Methoprene). IV. Soil Metabolism. J. Agr. Food Chem. 23:369-373.

50. Smith, R.A., W.S. Belles, K.W. Shen, and W.G. Woods, 1973. The Degradation of (N^3, N^3-Diethyl 2,4-dinitro-6-trifluoromethyl-m-phenylenediamine) in Soil. Pest. Biochem. Physiol. 3:278-288.

51. Stevenson, P.J. 1965. Gross Chemical Fractionation of Organic Matter. In: Methods of Soil Analysis. C.A. Black, D.D. Evans, J.L. White, L.E. Ensminger, and F.E. Clark (ed). Amer. Soc. Agron. Publ. No. 9. Madison, WI. pp. 1409-1421.

52. Anderson, J.R. 1973. A System for Evaluating Effects of Pesticides on Soil Microbial Activity. Bull. Ecol. Res. Comm. 17:470-472. (Now: Ecol. Bull., Swed. Nat. Res. Council).

53. Balandreau, J., and Y. Dommergues. 1973. Assaying Nitrogenase (C_2H_2) Activity in the field. Bull. Ecol. Res. Comm. 17:247-254. (Now: Ecol. Bull., Swed. Nat. Res. Council).

54. Bohool, B.B., and E. L. Schmidt. 1973. A Fluorescent Antibody Technique Determination of Growth Rates of Bacteria in Soil. Bull. Ecol. Res. Comm. 17:336-338. (Now: Ecol. Bull. Swed. Nat. Res. Council).

55. Casida, L.E., Jr. 1968. Methods for the Isolation and Estimation of Soil Bacteria. In: The Ecology of Soil Bacteria. T.R.G. Gray and P. Parkinsen (eds). University of Toronto Press, Toronto, Canada. pp. 97-122.

56. Curl, E.A., and R. Rodriguez-Kabana. 1971. Microbial Interactions. In: Research Methods in Weed Science, R.E. Wilkinson ed. S. Weed. Sci. Soc. PCP Enterprises, Inc. Atlanta, GA. pp. 163-194.

57. Gray, T.R.G., P. Baxby, I.R. Hill, and M. Goodfellow. 1969. Direct Observations of Bacteria in Soil. In: The Ecology of Soil Bacteria, T.R.G. Gray and J. Parkinsen (eds). University of Toronto Press, Toronto, Canada.

58. Jensen, V. 1969. The Plate Count Technique. In: The Ecology of Soil Bacteria, T.R.G. Gray and P. Parkinsen (eds). University of Toronto Press, Toronto, Canada.

59. Knowles, R.R., R. Brouzes, and P.O. Toole. 1973. Kinetics of Nitrogen Fixation and Acetylene Reduction, and Effects of Oxygen and of Acetylene on These Processes, in a Soil System. Bull. Ecol. Res. Comm. 17:255-262. (Now: Ecol. Bull., Swed. Nat. Res. Council).

60. Matulewich, V.A., P.F. Strom, and M. S. Finstein. 1975. Length of Incubation for Enumerating Nitrifying Bacteria in Various Environments. App. Microbiol. 29:265-268.

61. Ou, L.-T, D.F. Rothwell, W.B. Wheeler, and J.M. Davidson. 1978. The Effect of High 2,4-D Concentrations on Degradation and Carbon Dioxide Evolution in Soils. J. Environ. Qual. 7:241-246.

62. Pochon, J., and P. Tardieux. 1968. Enrichment Techniques and the Elective Cultivation of Bacteria. In: The Ecology of Soil Bacteria, T.R.G. Gray and D. Parkinsen (eds). University of Toronto Press, Toronto, Canada. pp. 123-137.

PRELIMINARY STUDIES EVALUATING COMPOSTING AS A MEANS FOR PESTICIDE DISPOSAL

Donald E. Mullins, Department of Entomology
Julie A. Petruska, Agricultural Engineering
Robert W. Nicholson, Environmental Sciences and Engineering
Eldridge R. Collins, Jr., Agricultural Engineering
Rodney W. Young, Biochemistry and Nutrition

Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

ABSTRACT

A benchtop composter has been designed and constructed to provide laboratory data on the fate of hazardous wastes subjected to composting conditions. Preliminary studies using unlabeled pesticides have indicated this process might be quite useful in disposing of certain hazardous materials. For example, 79% of Diazinon was lost when composted in a 150 g mixture of dairy cattle manure and sawdust for 10 days and 68% chlordane was lost in 16 days when composted in 10 g composting media.

Introduction

A major problem often associated with pesticide usage is the suitable disposal of unused concentrated and dilute formulations of pesticides and pesticide-contaminated products. Since pesticides are used extensively in U.S. agriculture, there is need for abatement and control of pesticide buildup in the environment. Various methods of hazardous waste disposal currently being researched include incineration, biological treatment, physical-chemical conversion and land disposal methods (Wilkinson et al (12)). Some recent reports on biological disposal methods using disposal pits (Johnson and Baker (6), Egg et al (3)) and agricultural waste lagoons (Collins et al (1)) indicate these processes might be useful under certain conditions. However, information regarding the effectiveness of biological methods on a full scale basis is insufficient. There are several pesticide classes which have not been studied to determine their potential susceptibility to biological disposal (Wilkinson et al (12)).

It is conceivable that a technology involving microbial degradation could prove to be an effective, low cost means for disposing of unwanted pesticide materials and residues. Biological degradation of hazardous materials is not a new concept. It is well known that given time and appropriate conditions, most organic compounds will be metabolized by living systems. Microbes have assumed ever-increasing importance in studies concerned with pesticide degradation; and systems capable of supporting large microbial populations such as soil, water, and sewage, have long been thought to be ideal sites for pesticide degradation (Johnsen (4)). Unfortunately, the volatilization rate and extent of pesticide degradation for complex biological systems is not well understood.

It has been pointed out that composting of pesticide wastes might be quite effective, but has not been studied in sufficient detail (Wilkinson, et al (12)). A major problem with research on composting of pesticides involves technical difficulties associated with analysis and identification of the degradation products. As a consequence, the environmental impact involving subsequent disposal of potentially toxic residual materials produced from composting is unknown.

Although composting is an ancient practice, it is increasing in importance as a means for solving some of our municipal waste problems (Poincelot (9); Parr et al (8)). The development of large scale sewage sludge composting technology was facilitated by using bench model composters in which composting conditions could be controlled and studied in detail.

Pioneering research on the effect of the compost process relating to pesticide disposal was done in the late 1960's using four pesticides (Diazinon, DDT, dieldrin and parathion) mixed with rice hulls and fruit and vegetable wastes (Rose and Mercer (10)). Although low concentrations of pesticides were used, significant loss of the parent materials was observed in about 50 days. Since that time, other studies concerned with hazardous substance degradation have been conducted using animal wastes, and sewage sludge alone or mixed with soil (Johnsen et al (5), Doyle et al (2); Tucker et al (11)).

Specific Objectives

The purpose of this research project is to develop detailed information regarding the fate of hazardous materials under composting conditions. The specific objectives include: 1) to develop a procedure to evaluate pesticide degradation in benchtop composters, 2) to study degradation of selected hazardous materials under controlled conditions, to determine not only the disappearance of the parent materials but also the formation of major degradation products, and 3) by means of laboratory and field studies, to evaluate the possibility of using composting as a method for disposing of small quantities of pesticides (less than 2 kg or less than 20 liters).

Approach

Presently, the major thrust of this project is centered around the development of benchtop composters, and experimental and analytical methods designed to examine the effectiveness of microbes in composting media in degrading hazardous materials. Techniques are now available which may allow for more rapid and thorough studies of the composting process on hazardous waste degradation. These are: 1) the use of benchtop composters which allow control of composting conditions on a small scale (maintenance of high temperatures, moisture and optimal air flow), and 2) the use of radioisotope methodology which allows measurement of small amounts of materials including virtually all carbon-containing compounds (primary, secondary, tertiary metabolites and CO_2). We are in the process of applying these combined techniques, representing a new approach for examining the fate of pesticides in compost. The requirement for only small amounts of radiolabeled pesticide materials and the potential for quantitative recovery and identification of metabolites and end products may make this approach quite useful in facilitating the development of this aspect of compost technology.

As indicated above, the experimental methodology to be used in these studies calls for the use of benchtop composters and laboratory procedures which will provide as complete information on the degradation process as possible. The general scheme of the composting procedure is illustrated in Figure 1. Agricultural wastes such as dairy cattle manure will be mixed with sawdust along with specific ^{14}C-labeled compounds prior to placement

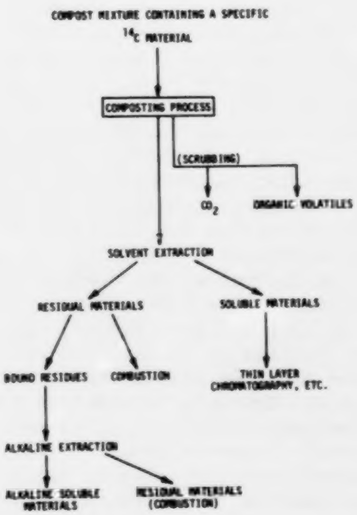


Figure 1. Compost Analysis Procedure

into the composting apparatus. During composting, $^{14}CO_2$ and ^{14}C-volatiles will be collected, and after incubation, the composted mixtures will be exhaustively extracted using conventional extraction techniques. Where feasible, identification or characterization of the reaction products will be made employing thin-layer, gas and liquid chromatographic analytical techniques. The following discussion outlines progress made in fulfilling the objectives of this research.

Results

Benchtop Composter

A series of benchtop composters modified from those described by Willson (13) have been assembled into one unit. Each unit consists of 6 sealed glass vials which act as the compost incubation chambers. Each vial is partially immersed in water contained in a 4 liter vessel. The temperature in the vessel is controlled by a circulating water bath which distributes heated water through Tygon tubing encircling the vessel (Figure 2). The assembly is housed in a specially constructed styrofoam container for insulation purposes.

The individual compost incubation chamber consists of a glass vial (50 ml capacity) with a stainless steel grid (16 mesh) held 1 cm above the bottom of the vial (Figure 3). Air is drawn into the bottom of the vial through the side arm, passes through the compost, and exits through the port at the top of the vial. The air then goes to volatile gas scrubbers which are polyurethane plugs for trapping organic volatiles and KOH scrubbers for trapping CO_2.

The system is designed in such a manner that up to 6 vials may be run at one time under constant temperature conditions. The intake air is humidified and heated to the same temperature as the vial to reduce the effects of cooling or dehydration of the composting media.

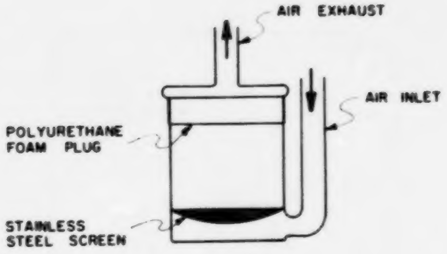


Figure 3. Compost Vial

The experimental conditions for composting in the benchtop composting apparatus are as follows: Equivalent (w/w) dairy cattle manure is mixed with sawdust (8-18 mesh) to achieve a moisture content of 60-65%. A 5 to 150 gram aliquot of this mixture is placed into the composting vial. The initial composting temperature is maintained at 35°C for 24 hours and is raised about 5°C each day until a final incubation temperature of about 65°C is reached. During the incubation, heated humidified air is drawn through the vial and compost for 1 minute at 10 minute intervals (50 ml/min).

The rate of CO_2 released from the incubation mixture is determined by titration of the KOH scrubbing solution (containing trapped CO_2) to a phenolphthalein end point, and can be used as an indicator of microbial activity. Figure 4 compares data of CO_2 released from 5, 10, and 15 gram compost mixtures.

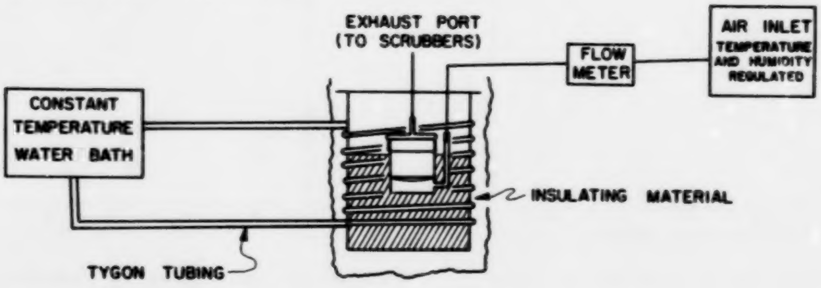

EXHAUST PORT (TO SCRUBBERS)
FLOW METER
AIR INLET
TEMPERATURE AND HUMIDITY REGULATED
CONSTANT TEMPERATURE WATER BATH
INSULATING MATERIAL
TYGON TUBING

Figure 2. Benchtop Composter Unit

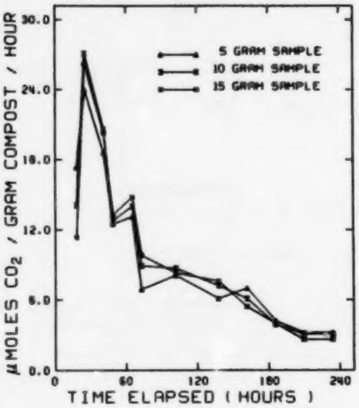


Figure 4. Comparison of CO_2 Release Rates from Compost.

Composting of Non-Radiolabeled Pesticides

Preliminary experiments designed to examine non-radiolabeled pesticide loss from compost were conducted using Diazinon and chlordane. The results of two of these experiments are presented here. Figure 5 illustrates results when about 100 ppm Diazinon was incubated in a 150 g sample of compost material for 10 days. It can be seen that the Diazinon level is reduced to 21 ppm after 10 days. Included in this figure is the rate of CO_2 released during the experiment. The rate decreased from about 14 μmole/g/h (40 h) to 4 μmole/g/h. Figure 6 illustrates the loss of chlordane (80 ppm) from 10 g compost material incubated for 16 days. The final concentration of chlordane was 30 ppm representing a loss of 68% of the parent compound. The rate of CO_2 release decreased from 21 μmole/g/h (24 h) to about 2.4 μmole/g/h (382 h).

Evaluation of Losses Due to Abiotic Factors

Since some of the losses observed might have been due to volatilization or chemical degradation, studies of the effects of abiotic factors such as temperature and humidity on pesticide loss have also been conducted in our laboratory. A series of experiments using Diazinon adsorbed onto glass or organic media (sawdust, cellulose), contained in sealed or open vials, in dry or humid environments at various temperatures have been performed. Table 1 presents data obtained when Diazinon was adsorbed onto a glass surface, allowed an avenue of escape (open versus closed vials) and incubated at various temperatures for 36 hours. The humidity was not controlled. It can be seen that the Diazinon level was stable in sealed or open vials when held at 0 or 24°C. However, at 65°C Diazinon loss from the glass surface was high in the open vial (2% recovery) and to a lesser extent in the sealed vial (74% recovery). Since the humidity was uncontrolled, and loss was

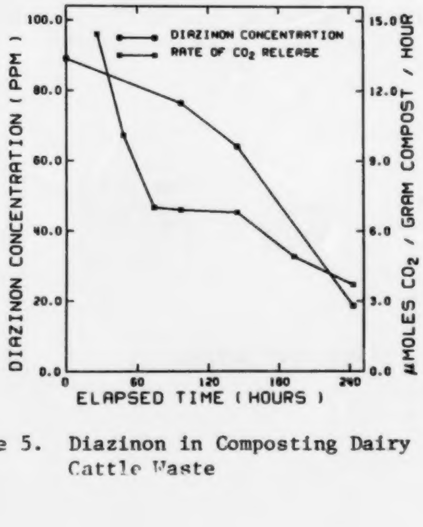


Figure 5. Diazinon in Composting Dairy Cattle Waste

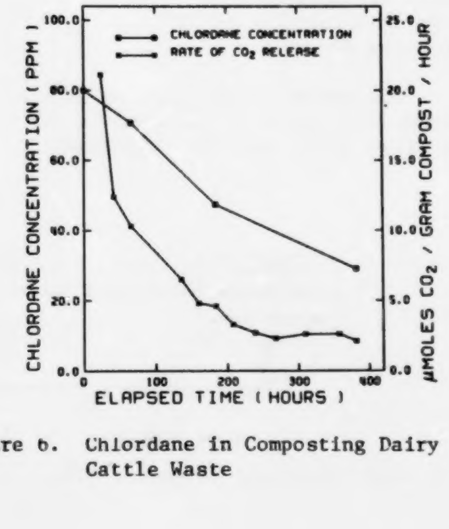


Figure 6. Chlordane in Composting Dairy Cattle Waste

TABLE 1. THE EFFECT OF TEMPERATURE ON DIAZINON LOSS FROM A GLASS SURFACE IN OPEN AND SEALED VIALS*

Time elapsed hours	Percent Recovery[#] 0°C open	0°C sealed	24°C open	24°C sealed	65°C open	65°C sealed
12	94	92	96	92	40	94
24	92	87	90	92	18	83
36	88	95	93	94	2	74

*Open and sealed vials placed in a humid environment.

[#] Initial concentration = 100 μg Diazinon.

observed in the sealed vial held at 65°C, it was hypothesized that the combined effects of temperature and humidity could have produced the observed Diazinon loss. Support for this hypothesis was obtained in an experiment designed to examine the effects of humidity on Diazinon adsorbed onto glass and incubated at 62°C for 36 hours. The results are presented in Table 2. The information presented in Tables 1 and 2 indicates that Diazinon loss from glass surfaces can be quite significant when held at temperatures above 62°C. These losses may be due primarily to volatilization, but in humid environments it is likely that some loss may be due to degradation (i.e. chemical hydrolysis).

The process of adsorption onto and absorption into organic media are involved when pesticides are applied to compost material. Therefore, the effects of temperature and humidity on the loss of Diazinon in the absence of significant microbial activity wereexamined in order to evaluate the Diazinon loss from organic media due to abiotic factors. The results of one such experiment are presented in Table 3. It can be seen that increases in temperature together with the presence of moisture result in loss of Diazinon from organic media.

The vials containing moisture (open and sealed) showed the greatest amount of Diazinon loss which suggests that the combined effects of increased temperature and humidity may result in Diazinon loss primarily by degradation.

The effects of heat and humidity on Diazinon in the composting apparatus with and without aerationwere studied in order to further evaluate losses which might be

TABLE 2. THE EFFECT OF HUMIDITY ON DIAZINON LOSS FROM A GLASS SURFACE IN OPEN AND SEALED VIALS INCUBATED AT 62°C FOR 36 HOURS

Replicate	Percent Recovery[#] Open Dessicated Env.	Open Humid env.	Sealed Dessicated env.
1	<5	<5	100
2	<5	<5	102
3	<5	<5	101

[#] Initial concentration = 81 μg Diazinon

TABLE 3. THE EFFECT OF TEMPERATURE AND HUMIDITY ON DIAZINON LOSS FROM AN ORGANIC MEDIA IN OPEN AND SEALED VIALS INCUBATED FOR 36 HOURS

Treatment [*]	Percent Recovery[#] 25°C	 45°C	 65°C
Sealed vial; desiccated env.	96±4	86±8	92±2
Open vial; desiccated env.	103±6	95±10	91±4
Sealed vial; humid env.[+]	96±7	82±3	60±5
Open vial; humid env.	91±3	89±5	61±1

[*] Diazinon applied to 1 g dry chromatographic grade cellulose.

[#] Initial concentration = 82 ppm Diazinon, mean ± standard deviation based on 3 replicates.

[+] Water saturated cotton plug suspended in vial.

incurred due to abiotic factors. A series of composting vials were set up in such a manner that dry and wet organic media was exposed to aerated (50 ml/min, 1 min. out of 10) and non-aerated conditions for 36 hours. The results are shown in Table 4. It can be seen that Diazinon recovery for dry, aerated and non-aerated media was higher than for the wet, aerated and non-aerated. Furthermore, losses in the wet, aerated media were greater than in the wet, non-aerated media. The information from this experiment indicates that humidity does result in increased Diazinon loss and that aeration in a humid environment results in greater loss. Experiments designed to further evaluate the effects of temperature, volatility and hydrolysis will be conducted using radiolabeled Diazinon.

TABLE 4. THE EFFECT OF AERATION AND HUMIDITY ON DIAZINON LOSS FROM ORGANIC MEDIA INCUBATED AT 65°C IN BENCH TOP COMPOSTERS FOR 36 HOURS

Treatment[*]	Percent Recovery[#]
Dry; aerated	81±5
Dry; non-aerated	81±3
Wet; aerated	46±4
Wet; non-aerated	57±0

[*] Dry treatment: 5 grams dry chromatographic grade cellulose, aerated with desiccated air.
Wet treatment: 12.5 grams wet chromatographic grade cellulose (60% H_2O), aerated with humid air.
Non-aerated units were sealed.

[#] Initial concentration: Dry treatment 92 ppm Diazinon
Wet treatment 96 ppm Diazinon
Mean ± standard deviation based on 3 replicates.

Studies on $^{14}CO_2$ Recovery

Studies on recovery of $^{14}CO_2$ released in the composting apparatus have been done in order to determine the efficiency of trapping this metabolite from composting material. Carbon dioxide is trapped in 5 N KOH and subsamples are distilled into ethanolamine and scintillation cocktail prior to scintillation counting as described by Mullins and Eaton (7). Results of these studies are presented in Table 5. Recovery of $^{14}CO_2$ resulting from release, capture, and subsequent distillation into the scintillation fluid was quite good. The presence of polyurethane plugs placed on line in front of the KOH scrubbers (used in trapping organic volatiles) does not interfere with the $^{14}CO_2$ trapping efficiency . It can also be seen from this table that CO_2-saturated KOH (saturated during the composting process) is also quite efficient in trapping $^{14}CO_2$. However, we have found that the scrubbing solutions must be changed frequently enough (every 24 hours) during a compost experiment to avoid over saturation which will result in decreased trapping efficiency.

Trapping of ^{14}C-Containing Volatiles on Polyurethane Plugs

In addition to examination of CO_2 trapping efficiencies in KOH, a preliminary study on trapping efficiencies of polyurethane plugs has been conducted. We have found that when ^{14}C-chlordane is completely volatilized off of a glass surface it is trapped (100% recovery) in polyurethane plugs contained in the compost vial. Additional studies of the polyurethane trapping efficiencies under composting conditions are in progress.

Conclusions

A benchtop composting apparatus has been designed and constructed which allows for composting of small samples of organic material. Preliminary studies indicate that when two pesticides, Diazinon and chlordane, are incorporated into composting dairy cattle manure, the pesticide level decreases. It does not appear that these losses are due primarily to volatility. However, humidity and temperature (abiotic factors) may contribute to the losses of the parent materials placed in a composting environment. The use of radiolabeled pesticide materials and the benchtop composting apparatus should provide useful information on the overall degradation process, including the formation and release of CO_2 and other metabolites.

TABLE 5. RECOVERY OF $^{14}CO_2$ RELEASED FROM $NA_2^{14}CO_3$ IN THE COMPOSTING APPARATUS

Treatment*	Number of Replicates	Percent Recovery
No compost present		
polyurethane plugs not on line	6	88.9 ± 3.9 s.d.
polyurethane plugs on line	6	96.5 ± 1.0 s.d.
Compost present#		
CO_2 - saturated KOH+	3	95.0 ± 0.8 s.d.
unsaturated KOH	3	88.0 ± 1.0 s.d.

*Initial activity $Na_2{}^{14}CO_3$ = .23 µCi/replicate, scrubbed for 1 hour.

#10 grams dairy cattle manure; sawdust mixture

+1.35 mmoles CO_2 reacted with KOH

References

1. Collins, E. R., Jr., J. A. Petruska, D. E. Mullins and R. W. Young. 1980. Animal waste lagoon systems for disposal of pesticide wastes. Paper No. 80-2112. Amer. Soc. Agri. Engin., St. Joseph, Michigan. 22 pp.

2. Doyle, R. C., D. D. Kaufman and G. W. Burt. 1978. Effect of dairy manure and sewage sludge on 14-C pesticide degradation in soil. J. Agr. Food Chem. 26:987-989.

3. Egg, R., R. L. Reddell and R. Avant. 1980. Disposal of waste pesticides in roofed and unroofed evaporation pits. Paper No. 80-2111. Amer. Soc. Agri. Engin. St. Joseph, Michigan. 15 pp.

4. Johnsen, R. E. 1976. DDT metabolism in microbial systems. Residue Rev. 61:1-28.

5. Johnsen, R. E., C. S. Lin, K. J. Collyard. 1971. Influence of soil amendments on the metabolism of DDT in the soil. Proc. IUPAC 2nd Internat. Congr. Pest. Chem., Israel 6:139-156.

6. Johnson, L. A. and J. L. Baker. 1980. Water and pesticide volatilization from pits used for disposal of dilute waste pesticides. Paper No. 80-2110. Amer. Soc. Agri. Engin. St. Joseph, Michigan. 27 pp.

7. Mullins, D. E. and J. L. Eaton. 1977. Labeled $^{14}CO_2$ production in response to light stimuli: a method and a preliminary investigation. Comp. Biochem. Physiol. 58B:365-375.

8. Parr, J. F., E. Epstein and G. B. Willson. 1978. Composting sewage sludge for land application. Agri. Environ. 4:123-137.

9. Poincelot, R. P. 1975. The Biochemistry and Methodology of Composting Bull. 754. Connecticut Agr. Exp. Station, New Haven, CT.

10. Rose, W. W. and W. A. Mercer. 1968. Fate of insecticides in composted agricultural wastes. Progress Report Part 1. National Canners Association, Washington, D.C. D-3049. 27 pp.

11. Tucker, E. S., V. W. Saeger and O. Hicks. 1975. Activated sludge primary biodegradation of polychlorinated biphenyls. Bull. Env. Cont. Toxicol. 14:705-713.

12. Wilkinson, R. R., G. C. Kelso, and F. C. Hopkins. 1978. State of the Art Report: Pesticide Disposal Research. USEPA Document. EPA-6001/2-78-183. August 1978. 225 pp.

13. Willson, G. B. 1971. Composting dairy cow waste. Proc. Internat. Symp. Livestock Wastes. Published by the Amer. Soc. Agri. Engin., St. Joseph, Michigan. pp. 163-165.

TOP SEALING TO MINIMIZE LEACHATE GENERATION - STATUS REPORT

Grover H. Emrich and William W. Beck, Jr.
SMC-MARTIN
King of Prussia, PA 19406

ABSTRACT

Remedial actions consisting of regrading and the placement of a 20 mil PVC membrane seal over a 10 hectare (25-acre) landfill was conducted at Windham, CT Landfill during the fall of 1979. A bimonthly monitoring program is being conducted to establish the effectiveness of the top seal for mitigation of the existing ground-water pollution. Investigations of the structural integrity of the top seal were conducted in April and May of 1980. These investigations indicated a minimal number of small punctures occurred in the top seal membrane. Spring recharge was effectively intercepted by the membrane and diverted from the landfill. Pan lysimeters installed below the membrane confirmed the effectiveness of the membrane for intercepting recharge from precipitation. Water samples from monitoring wells within the landfill and surrounding it indicate that water quality is improving and the plume of contamination is receding toward the landfill. It is concluded that it is possible to place a 20 mil PVC top seal over a 10 hectare (25 acre) landfill as a remedial measure to mitigate contamination of ground water.

INTRODUCTION

The development and implementation of a remedial action project designed to abate pollution from a landfill requires: 1) knowledge of the potential remedial actions, 2) site selection and documentation of the problems associated with the landfill, 3) design and construction of the remedial actions, and 4) monitoring to determine the effectiveness of the actions implemented. Knowledge of potential remedial actions was addressed and resulted in the publication of "Guidance Manual for Minimizing Pollution from Waste Disposal Sites" by A. L. Tolman, A. P. Ballestero, W. W. Beck and G. H. Emrich. The site selection process for the landfill resulted from the review of over 400 sites, field inspection of 50 sites, a detailed analysis of five sites, drilling and geophysical work at two and the final selection of the Town of Windham, CT Landfill. The Windham, CT Landfill located in east central Connecticut, is approximately 10 hectares (25 acres) in size and consists of two sections (see Figure 1). The landfill is located in an area of sand and gravel immediately adjacent to the City of Willimantic water supply reservoir and a Corps of Engineers flood control dam. The eastern (old) half of the landfill is approximately 4 hectare (10 acres) with its lower portion in the ground water. The western (new) landfill is approximately 6 hectare (15 acres) and is above the ground water. Local sands and gravels were used for cover material. The landfill operated

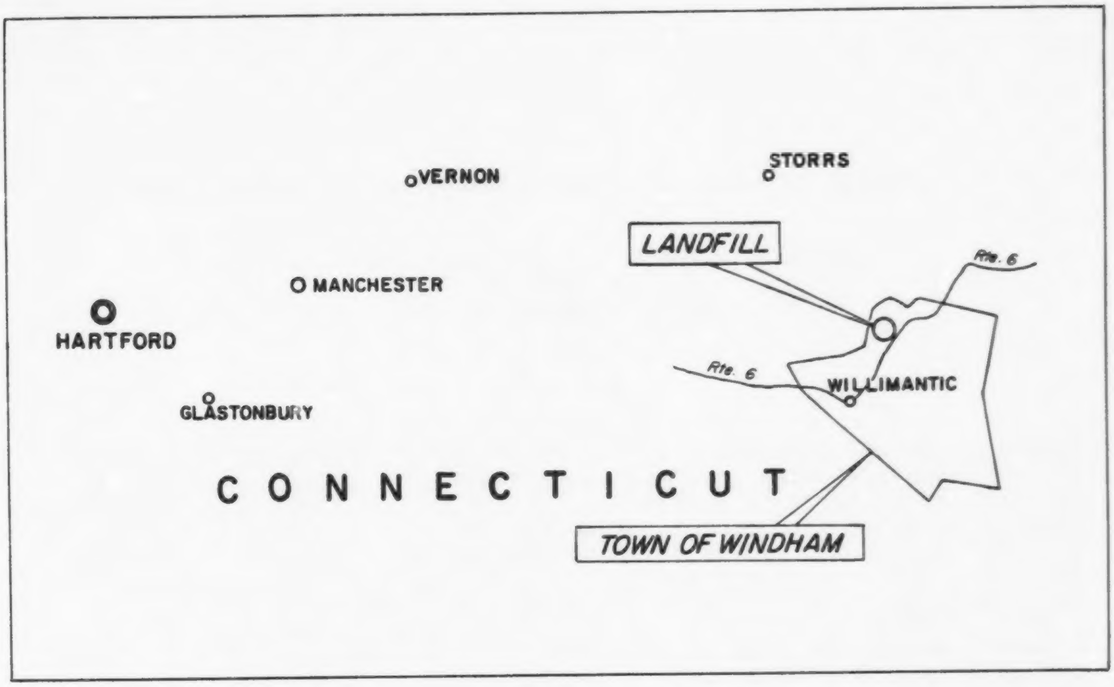


Figure 1. Location of the Windham Landfill, Windham, Connecticut.

from approximately 1945 to 1978. A series of monitoring points emplaced through and around the landfill has defined the area of ground-water pollution and its movement through time (see Figure 2).

Remedial actions proposed to abate and prevent pollution from the landfill included: 1) regrading of the landfill to maximize surface water runoff and minimize infiltration, 2) the placement of a 20-mil PVC top seal, 3) covering the top seal with approximately 18 inches of final cover, and 4) revegetation (see Figure 3). The remedial actions were designed to be passive to insure minimum future maintenance. From the late summer to the early winter of 1979, these remedial actions were implemented at the site and final revegetation was accomplished in the spring of 1979.(1)

Before the remedial actions began, a detailed monitoring network was established to develop information pertinent to the reaction of the landfill to precipitation events prior to the remedial actions and then after completion of the remedial actions to evaluate their effectiveness. This monitoring network included: 1) the emplacement of suction and pan lysimeters in the refuse above the water table and in the surrounding soils to determine the reaction (infiltration) of the landfill to precipitation events, 2) the emplacement of piezometers into the water table below and around the landfill to determine the quantity and quality of leachate being generated and its movement through the subsurface, 3) the establishment of surface water sampling points, 4) the placement of suction lysimeters to obtain leachate in the refuse above the water table, and 5) the implementation of a bimonthly sampling program to determine changes in the geometry of the pollutional plume with time.

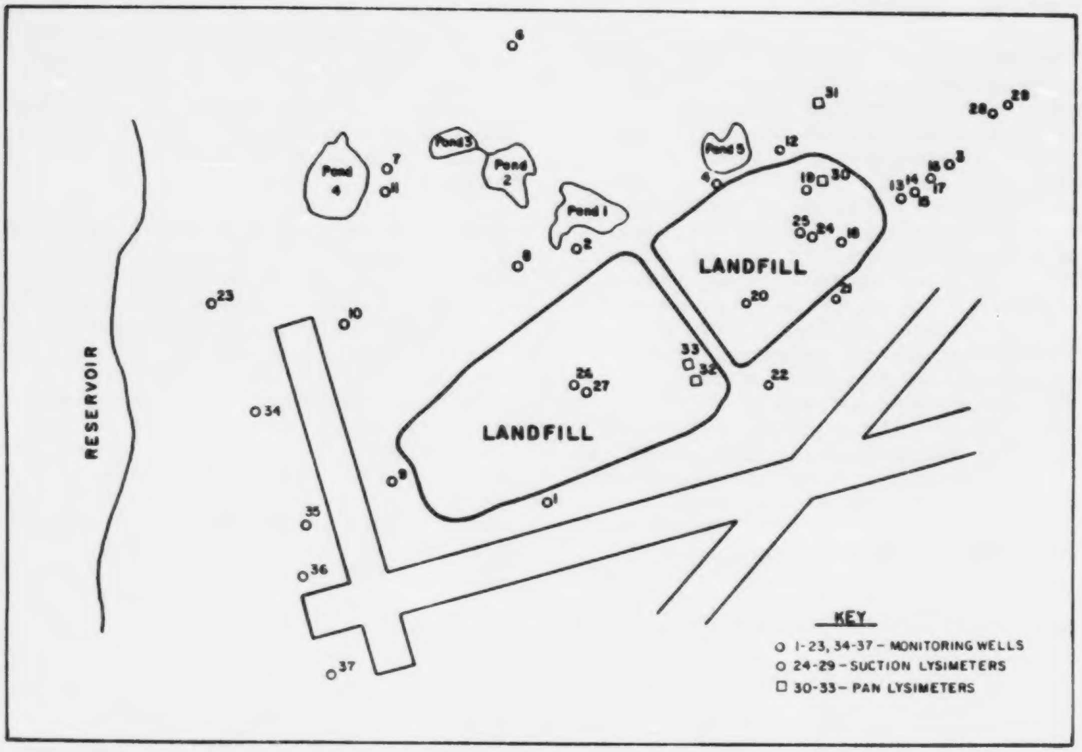

RESERVOIR
Pond 4
Pond 3
Pond 2
Pond 1
Pond 5
LANDFILL
LANDFILL
6
31
28
29
7
11
12
4
19
30
13
14
15
3
17
25
24
16
2
8
21
20
23
10
33
32
22
26
27
34
9
1
35
36
37
KEY
○ 1-23, 34-37 – MONITORING WELLS
○ 24-29 – SUCTION LYSIMETERS
□ 30-33 – PAN LYSIMETERS

Figure 2. Location of monitoring points at the Windham Landfill, Windham, Connecticut.

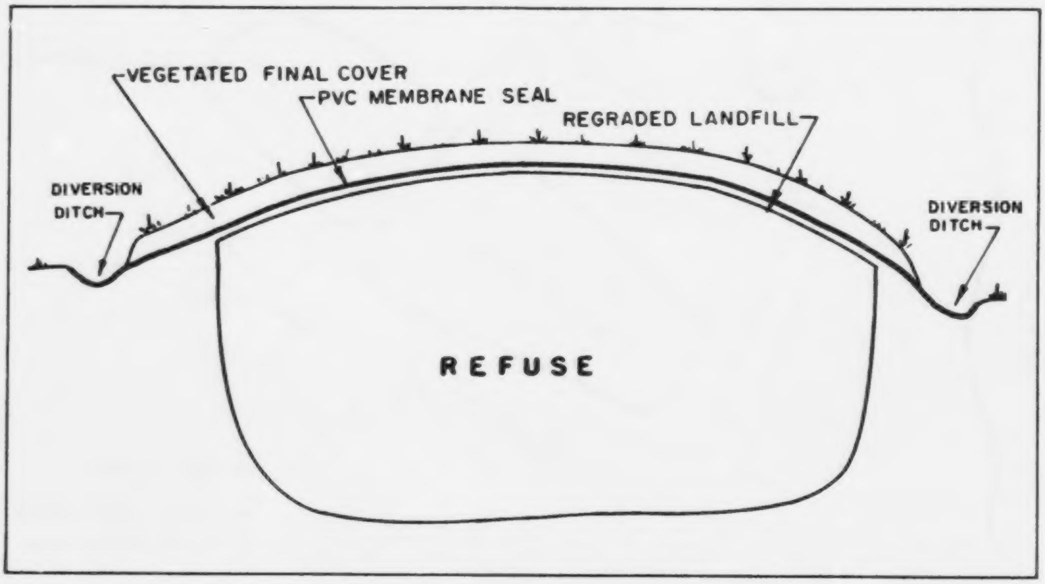

VEGETATED FINAL COVER
PVC MEMBRANE SEAL
REGRADED LANDFILL
DIVERSION DITCH
DIVERSION DITCH
REFUSE

Figure 3. Typical section through the Windham Landfill.

TOP SEAL INTEGRITY

The 20 mil PVC membrane seal with solvent welded seams was placed over the 10 hectare (25 acre) Windham Landfill in the fall of 1979. Immediately beneath the membrane are 10 cm (4 in) of compacted fine grain sand washings. The membrane was covered with an average of 50 cm (18 in) of local fine sand and gravel which was spread in 15 cm (6 in) layers and revegetated. In April 1980 an investigation of selected areas was conducted at the site to determine the membrane's integrity. Seven excavations (test pits) were made by hand through the cover material to the membrane in both the old and the new sections of the landfill (see Figure 4). It was determined that the membrane maintained its integrity during the placement of the cover material. Although there were numerous indentations up to 4 cm (1-1/2 in) deep in the membrane, there was no evidence of puncture. These indentations were caused by the final cover material which consisted of both sand and gravel.

The thickness of the cover material on the eastern (old) landfill varied from 10 to 46 cm (8 to 18 in). On the western section of the landfill (new) final cover varied from 38 to 46 cm (15 to 18 in). During the placement of the cover material over the seal, truck traffic patterns had to be established to assure a logical and systematic completion of the project. Several areas of high truck traffic were selected for investigation (see Figure 4). Test Pits #1 and #2 were located in the

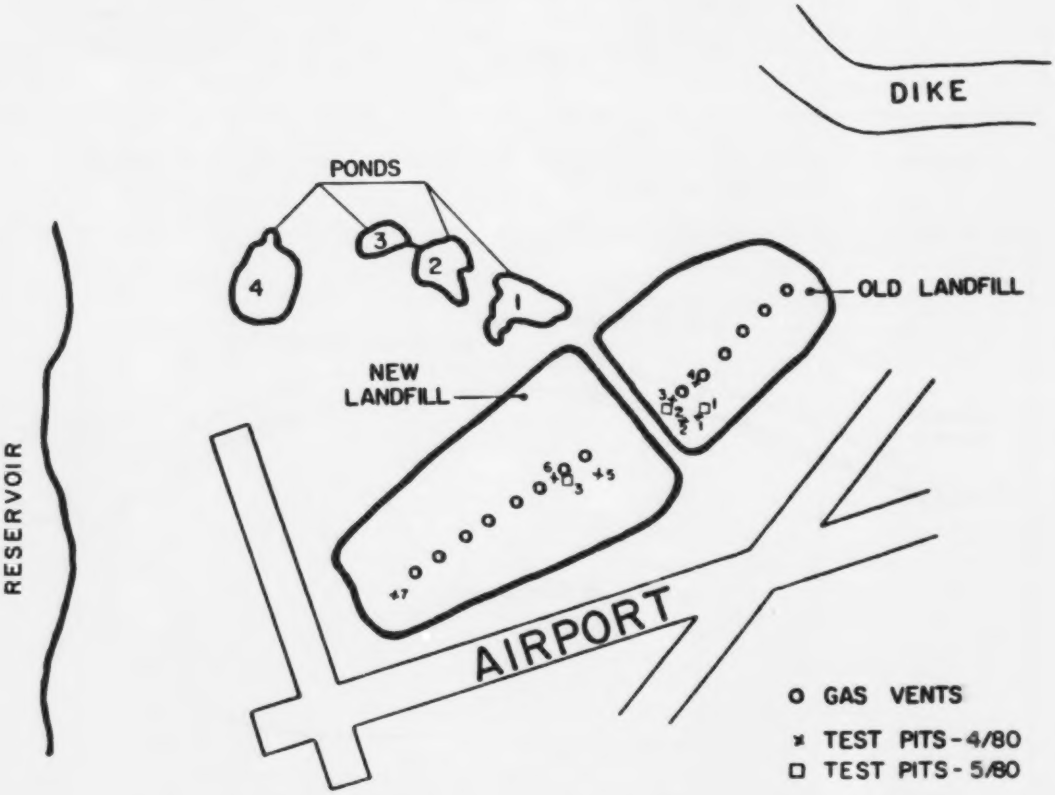


Figure 4. Location of test pits for Top Seal Integrity Tests.

area of heavy truck traffic and it was expected that these would be the most likely areas for puncture or tearing of the membrane. Test Pit #5 was dug in an area in which there was significant evidence on the surface of heavy truck traffic. The results of this investigation showed no visible punctures in the seal.

In the week previous to this investigation, there had been a 13 cm (5 in) rain over a five to six hour period, which caused local flooding. The rain eroded sections of the cover material in the swale between the two sections of the landfill as well as on the northwest side of the new landfill. Exposed areas were up to 2 m (6 ft) wide and 9 m (30 ft) long. Careful examination of these indicated no loss of integrity of the membrane.

In May 1980, the integrity of the membrane was again inspected by staff members from EPA and the U. S. Corps of Engineers Waterways Experimental Station, Vicksburg, Mississippi. Three additional test pits were dug on the two sections of the landfill. Test Pit #1 was approximately at the same location as Test Pit #1 dug in April 1980 (see Figure 4). At this pit there was 35 to 38 cm (14 to 15 in) of cover material and numerous indentations in the top of the membrane. Test Pit #2 was located in the same approximate area as Test Pit #3 from the April 1980 investigation. Cover consisted of sand with some gravel and was 23 cm (9 in) thick. Test Pit #3 was dug on the new landfill to the east of Test Pit #6 dug in April 1980. Cover material consisted of sand with some gravel and was 30 cm (12 in) thick.

Sections of the membrane seal were removed for testing by the Waterways Experimental Station from Test Pits #2 and #3. The membrane was patched using similar material and solvent welds. Several breaks in the membrane recovered from Test Pit #3 were observed when it was held up to the light with the maximum break being one-quarter of an inch in length. All of the breaks were produced by punctures from the top down. It was noted that water was seeping into Test Pit #3. This was from spring recharge (rain) which moved down to the membrane and then moved horizontally along the membrane. The membrane removed from Test Pit #2 contained no punctures. The membrane could not be removed from Test Pit #1 as it was covered by water. The water was from 1 to 2 cm (0.5 to 0.75 in) deep resulting from obvious seepage of infiltrated water down through the cover material to the membrane with movement along the membrane-cover material interface. The membrane was carefully observed in this test pit for three hours. There was no evidence of air bubbling through the water which would indicate the breaks in the membrane.

It was concluded from these studies that even in areas of heaviest truck traffic there were only a few breaks in the membrane and these breaks did not significantly reduce the effectiveness of the membrane to stop the movement of water in the cover material. Therefore, it was concluded that the majority of the infiltration was moving down to the membrane and then moved horizontally across the surface of the membrane discharging at the edges of the refuse into a lined drainage swale.

MONITORING

In the fall of 1978, a monitoring program was implemented to determine the impact of the refuse on the underlying ground water from precipitation events. Suction lysimeters were placed in the refuse to determine the passage of moisture (leachate) through the landfill. In order to determine the quantity of moisture moving through the landfill, four pan lysimeters were emplaced, three with collection areas of 0.4 m^2

(4 square feet) and the fourth with a collection area of 2.3 m^2 (25 square feet) in order to provide cross correlation of data between the smaller and larger collection areas. Wells were installed in and below the landfill to further assess leachate quality and its impact on water quality. Wells were also located upgradient and downgradient from the landfill to determine the movement contamination from the landfill. Adjacent ponds were sampled as well as the adjacent water supply reservoir to determine the effect of the landfill on these bodies of surface water (see Figure 2).

Between February and June 1979, wells, ponds and lysimeters were sampled on a monthly basis to determine water quality. The water levels in the wells and ponds were measured weekly and the volume of water collected in the pan lysimeters was measured. This program indicated leachate of moderate strength was generated by the old fill whereas leachate of somewhat higher strength was generated by the newer portion of the landfill. Leachate was found to effect the ground water downgradient of the fill. There was significant contrast between the background water quality measured upgradient and that of contaminated ground water found downgradient of the landfill. Analysis of the results of the weekly monitoring of ground water and surface water elevations and daily precipitation data verified significant infiltration was taking place in to the landfill. As much as 85 percent of the water passing through the refuse was derived from infiltration of precipitation.

Beginning in the fall of 1979, with the installation of the seal, bimonthly sampling was instituted at selected monitoring points. Results of the sampling showed that the impact of the landfill on ground water has been mitigated between November 1979 and November 1980. Visual observation shows that coloration in the ponds adjacent to the landfill had improved significantly. Analysis for water samples collected bimonthly had shown improvement in the ground water as well as retreat of the leachate plume.

In November 1979, specific conductivity (see Figure 5) indicated a major plume moving westward toward the reservoir as well as the secondary plume moving northward towards Ponds 1, 2 and 3. By November 1980, the secondary plume had withdrawn toward the landfill and the major westward plume had been narrowed. In the summer of 1980, four additional wells were drilled on the western side of the landfill to better define this plume. Comparison of most specific conductivity values in November 1979 with those of November 1980 have shown a decrease in the specific conductivity indicating a decrease in the amount of leachate generated.

The volume of water collected in the pan lysimeters was measured during the bimonthly sampling rounds. The background pan lysimeter responded normally to precipitation events. Little or no water was collected from the pan lysimeters below the membrane seal indicating that the top seal is effectively controlling infiltration into the landfill from precipitation events.

CONCLUSIONS

A 20 mil PVC top seal can successfully be placed over a 10 hectare (25 acre) landfill based on the results of liner integrity tests. The 20 mil PVC membrane maintained its flexibility during the placement of cover material which contained coarse fragments. A series of test pits excavated by hand to the membrane showed that only a few punctures were present in areas which experienced high truck traffic during placement of the cover material. The few punctures that were present were all from the top down and were less than 2.5 cm

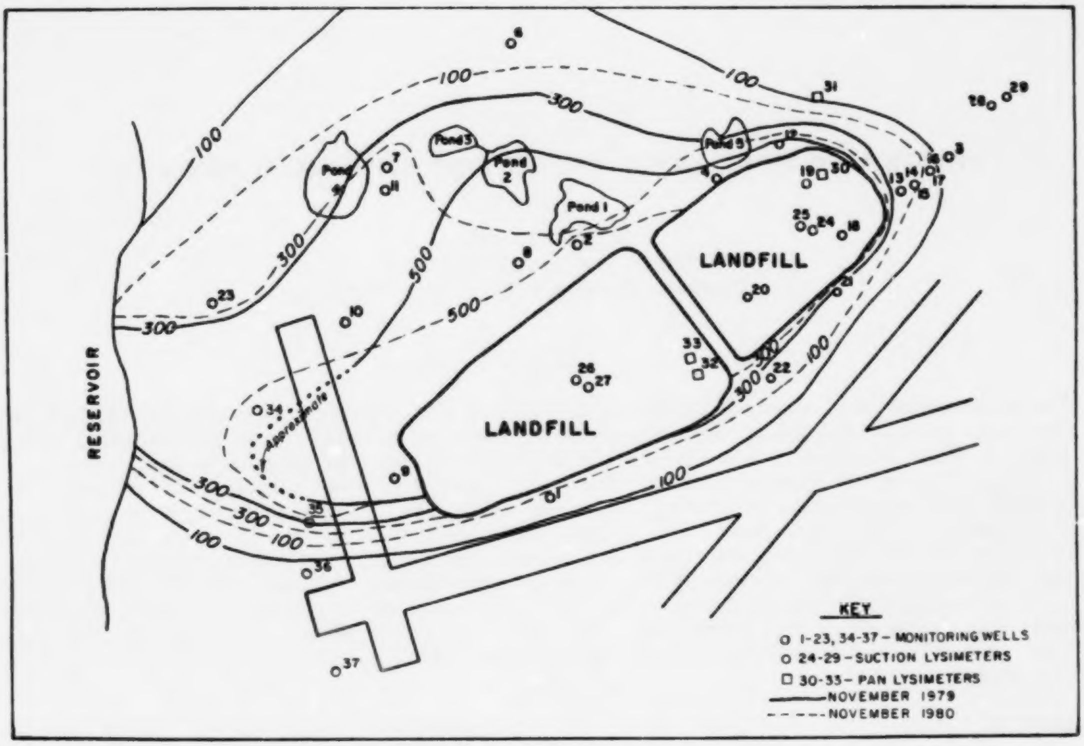

RESERVOIR
LANDFILL
LANDFILL
Pond 1
Pond 2
Pond 3
Pond 4
Pond 5
Approximate
100
300
500
KEY
○ 1-23, 34-37 – MONITORING WELLS
○ 24-29 – SUCTION LYSIMETERS
☐ 30-33 – PAN LYSIMETERS
——— NOVEMBER 1979
- - - - NOVEMBER 1980

Figure 5. Specific conductivity in November 1979 and November 1980.

(1 in) length. The test pits constructed to the top seal indicated that the spring recharge was intercepted by the membrane seal and moved water laterally to the line diversion ditches surrounding the landfill. Pan lysimeters placed below the top seal confirmed that little or no precipitation moves through the top seal. Specific conductivity tests made of the lysimeters and wells at the site show that the plume of contamination resulting from the landfill is receding toward the landfill and concentrations in the vicinity of the landfill are decreasing. Based on the results of these investigations, one year of monitoring data, it is concluded that the top seal is effectively controlling the infiltration of precipitation to the landfill and significantly reducing the contamination effects of the site.

REFERENCES

1. Emrich, Grover H., Beck, William W., Jr. and Tolman, Andrews L. Top Sealing to Minimize Leachate Generation, Case Study of the Windham, CT Landfill.

INVESTIGATION OF THE LIPARI LANDFILL USING GEOPHYSICAL TECHNIQUES

Joseph R. Kolmer
Woodward-Clyde Consultants
Plymouth Meeting, Pennsylvania 19462

ABSTRACT

The implementation of a remedial program at a landfill site requires a good understanding of site conditions as well as knowing the patterns of contaminant movement from the identified source area. In order to acquire this basic information needed for remedial program design, a two phase investigative program is recommended. The initial qualitative phase identifies the nature of the problem, and the quantification phase provides the design data. This paper discusses the qualitative investigation of the LiPari Landfill site in Gloucester County, New Jersey. This work was conducted as part of the U.S. Environmental Protection Agency remedial action research program. Geophysical techniques were used extensively in this survey and provided information on locations of buried metallic wastes within the landfill as well as the areal extent of contamination in the groundwater system downgradient of the landfill site. The use of geophysics at the LiPari site has provided a significant amount of data from which a quantification program for the site can be very effectively formulated.

INTRODUCTION

In June of 1980, the U.S. Environmental Protection Agency (US-EPA), Municipal Environmental Research Laboratory, Cincinnati, Ohio, awarded a research contract to Woodward-Clyde Consultants (WCC) for the preparation of a manual on how to select and implement remedial action programs for hazardous waste landfill sites. The methodology and documentation for preparation of this manual was to be developed by implementing a remedial program at the LiPari Landfill site in Gloucester County, New Jersey. The landfill site investigation would be conducted in three phases, the first of which being a qualitative site assessment, and the second a quantitative assessment from which a remedial program would be selected and preliminarily designed. The final phase would consist of implementation of the design remedial system. The total term of the research project is four years.

This paper contains a discussion of the first program phase, the qualitative investigation. Site history, existing site conditions and documented pollution conditions resulting from landfill discharge will be presented. Further, a discussion of various geophysical investigation techniques will be presented and their utility in subsurface investigations at landfill sites will be demonstrated. The information base for this paper was obtained from the files of the US-EPA in Cincinnati, Ohio, and Edison, New Jersey. The files of the Gloucester County Planning Department were also reviewed for applicable information. Further, the described geophysical surveys were conducted on site, and the results of the survey were reduced and interpreted by the WCC project staff.

BACKGROUND

The LiPari Landfill is located in Mantua Township, Gloucester County, New Jersey (see Figure 1). This landfill has been the subject of strong controversy, court proceedings, and limited investigative studies since the early 1970s. This activity stems from the fact that the landfill has been sited as a major source of surface water and groundwater pollution in the Gloucester County area.

The total LiPari property is approximately 18 hectares in size and is detailed in Figure 2. The topography can be categorized as gently rolling, except in the vicinity of the surface drainage patterns where the slopes steepen. Surface soils consist of sandy materials and, based on a preliminary review of the site

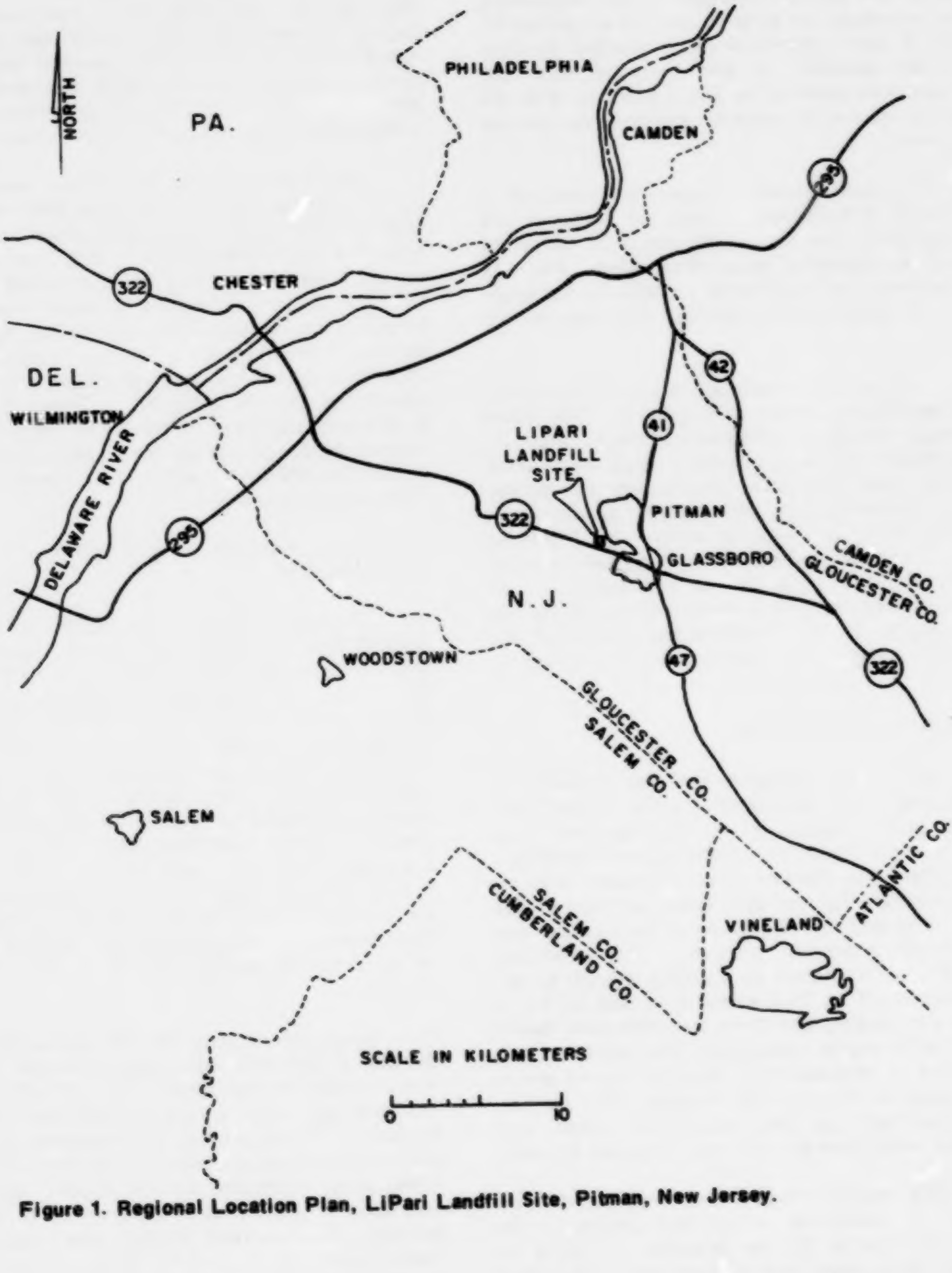

NORTH
PA.
PHILADELPHIA
CAMDEN
295
322
CHESTER
DEL.
WILMINGTON
DELAWARE RIVER
295
42
41
LIPARI
LANDFILL
SITE
PITMAN
322
GLASSBORO
CAMDEN CO.
GLOUCESTER CO.
N. J.
47
322
WOODSTOWN
GLOUCESTER CO.
SALEM CO.
SALEM
ATLANTIC CO.
SALEM CO.
CUMBERLAND CO.
VINELAND
SCALE IN KILOMETERS
0
10

Figure 1. Regional Location Plan, LiPari Landfill Site, Pitman, New Jersey.

conditions, it is believed that a large portion of the precipitation infiltrates to the subsurface.

The major land use in the area is agricultural. Relatively large apple and peach orchards are planted throughout the surrounding area, including the area of the LiPari property. There is also a peach orchard planted directly over the landfill. It was reported that this orchard was planted by Mr. LiPari to test the possible effects of methane gas and leachate on the trees.

The landfill itself occupies 2.4 hectares of the total 18 hectares. These 2.4 hectares are divided into two flat lying areas of differing elevation, separated by a steep slope. There is no evidence of extensive erosion or development of runoff flow channels over the landfill area.

Two surface drainage systems flow near the landfill, as shown in Figure 2. The main drainage pattern, Chestnut Branch, has its headwaters above the landfill area and, after flowing past the site, discharges to Alcyon Lake, approximately 370 meters downstream. Rabbit Run, a small tributary to Chestnut Branch, derives its headwater flow from a small spring located adjacent to the landfill. As shown in Figure 2, this stream flows along the full length of the northwestern edge of the landfill before it discharges to Chestnut Branch.

DISPOSAL OPERATIONS

Mr. LiPari obtained the site property in 1958, and soon thereafter started a sand and gravel quarry operation. It was reported that, shortly after initiation of the quarry operation, Mr. LiPari also started to accept waste materials as backfill for the excavated portions of the site. Apparently, the disposal operations followed the quarrying pattern. The sand and gravel were removed by cutting trenches, approximately 9 to 15 meters wide and 15 to 25 meters in length, and these trenches were backfilled with waste materials. The depth of the trenches is disputed, but reported values are in the range of two to five meters. The nonsalable portions of the excavated sands and gravels were used to cover the disposed wastes.

The wastes ranged from municipal type refuse to industrial solids and liquids. No detailed records of the quantity or types of wastes were kept, but it has been estimated that approximately 9,200 cubic meters of solids were buried and approximately 11.000 cubic meters of liquids were disposed. The liquids are thought to be largely uncontained. It was reported that drums of liquids brought to the site were drained into the landfill and the drums were reclaimed. Only the nonsalvageable drums were disposed. The volume of liquids transferred to the site in bulk, if any, is not known. Some of the reported wastes include cleaning solvents, paint thinners, paints, dirty waste solvents, phenols or amines wastes and residues, and resins or esther press cakes.

The only reported significant events during the period of landfill operation were two fires in 1969, and these fires were associated with the drummed wastes. The first fire occurred when a drum was being emptied into the fill, and the second occurred when a bulldozer struck a drum supposedly containing explosive wastes. There were reportedly three drums of explosive materials, and the disposition of the remaining two is unknown. These remaining drums are presumed to be in the landfill. Following these incidents, Mr. LiPari would not accept liquids for disposal. The landfill operations were ceased in 1971.

GEOLOGIC AND GROUNDWATER CONDITIONS

The LiPari Landfill is located within the central Upland subprovince of the coastal plain physiographic province. This region of Gloucester County is underlain by unconsolidated to poorly consolidated late Cretaceous and Tertiary age fluvial and marine deposits. The surficial deposits in the site area consist of upper Miocene (late Tertiary) age sands and gravels belonging to the Cohansey sand formation. Lying unconformably beneath the Cohansey are silty and clayey sands of the middle Miocene age, Kirkwood Formation. The thicknesses of the Cohansey Sand and Kirkwood Formations, as reported in the literature, are from 30 to 75 meters and 40 meters, respectively.

Some information on the subsurface conditions at the site was obtained from drilling work conducted by others during 1979. Four test borings were drilled, located as shown in Figure 2. These borings were reportedly cased and screened to a depth of six meters. The completion methods, screen depths, etc., are not known. Based upon the logs of these test borings, a subsurface profile was constructed and is shown in Figure 3. Strata 1 and 2 are probably the Cohansey Sand and are approximately 8 to 11 meters thick. Stratum 3 is in the Kirkwood and consists of two to five meters

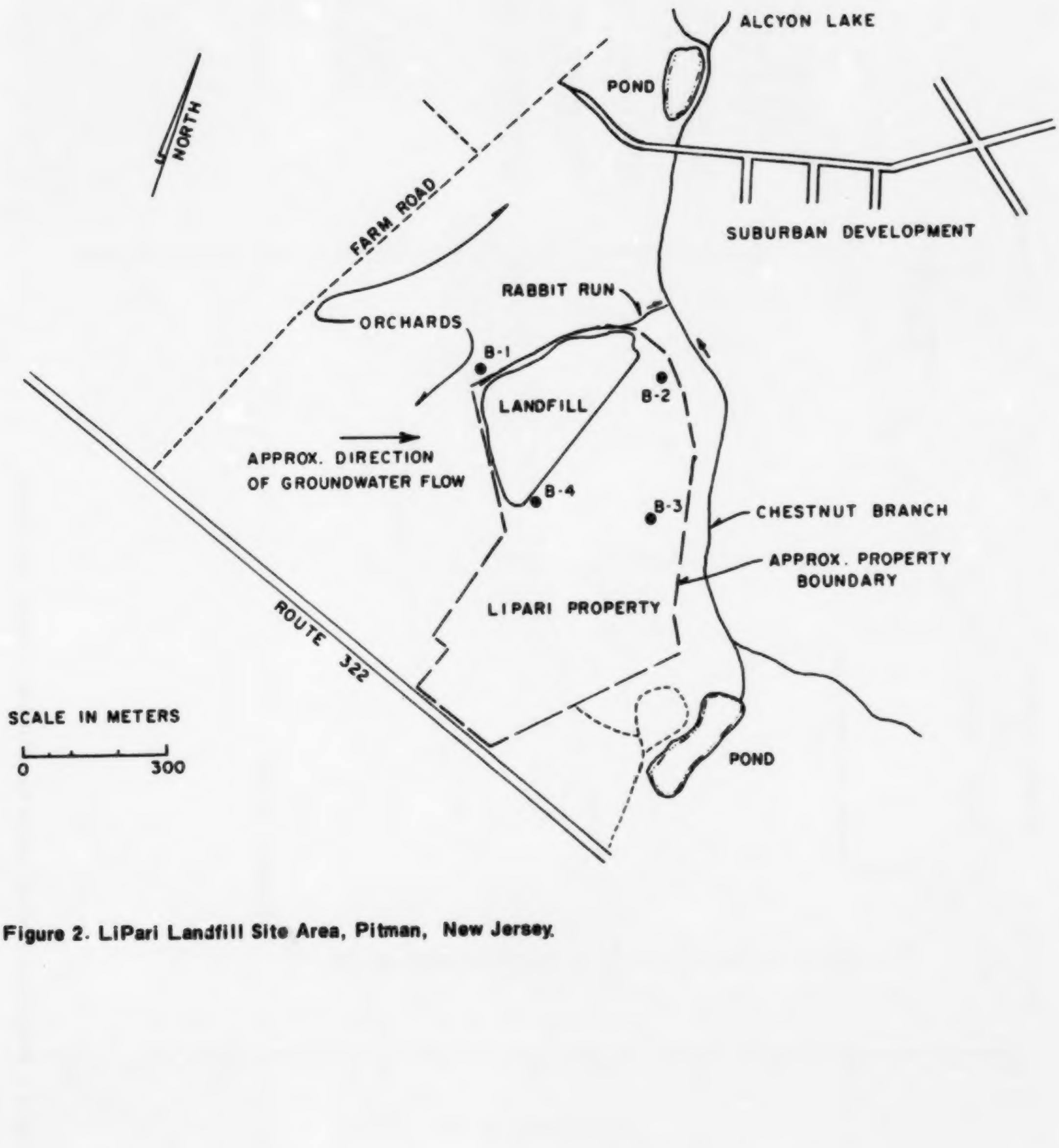

ALCYON LAKE
POND
NORTH
FARM ROAD
SUBURBAN DEVELOPMENT
RABBIT RUN
ORCHARDS
B-1
B-2
LANDFILL
APPROX. DIRECTION OF GROUNDWATER FLOW
B-4
B-3
CHESTNUT BRANCH
APPROX. PROPERTY BOUNDARY
LIPARI PROPERTY
ROUTE 322
SCALE IN METERS
0
300
POND

Figure 2. LiPari Landfill Site Area, Pitman, New Jersey.

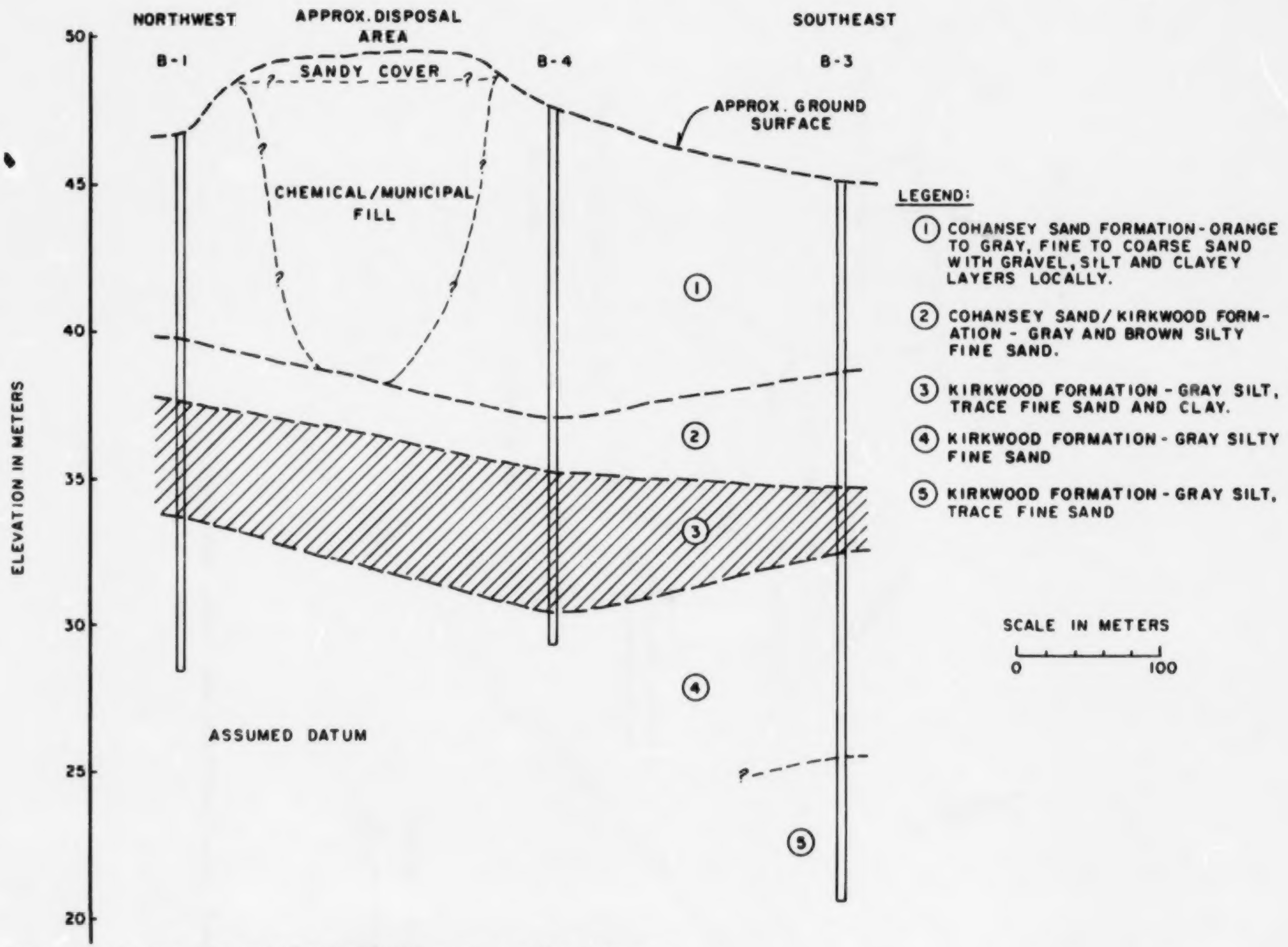

NORTHWEST
APPROX. DISPOSAL AREA
SOUTHEAST
B-1
B-4
B-3
SANDY COVER
CHEMICAL/MUNICIPAL FILL
APPROX. GROUND SURFACE
ASSUMED DATUM
ELEVATION IN METERS
50
45
40
35
30
25
20
①
②
③
④
⑤
?
LEGEND:
① COHANSEY SAND FORMATION - ORANGE TO GRAY, FINE TO COARSE SAND WITH GRAVEL, SILT AND CLAYEY LAYERS LOCALLY.
② COHANSEY SAND/KIRKWOOD FORMATION - GRAY AND BROWN SILTY FINE SAND.
③ KIRKWOOD FORMATION - GRAY SILT, TRACE FINE SAND AND CLAY.
④ KIRKWOOD FORMATION - GRAY SILTY FINE SAND
⑤ KIRKWOOD FORMATION - GRAY SILT, TRACE FINE SAND
SCALE IN METERS
0
100

Figure 3. Subsurface Profile, LiPari Landfill Site, Pitman, New Jersey.

of medium dense gray clayey silt and fine sand. The lowermost deposits (Strata 4 and 5), encountered from depths of 15 to 20 meters, consist of medium dense, gray, fine sandy silt/silty fine sand. All four test borings terminated within the Kirkwood Formation.

The preliminary geologic assessment of the site indicated that near surface groundwater would occur in the Cohansey Sand above the Kirkwood Formation. The clayey silts in the Kirkwood would tend to limit vertical movement of the groundwater. The relationship between horizontal and vertical flow is dependent upon the relative hydrogeologic characteristics of the Cohansey and Kirkwood units and their interaction with the nature of the chemical contaminants at the site. These relationships would be detailed during the follow-on quantitative assessment of the existing site conditions.

Groundwater level measurements taken from the four existing wells at the site indicated that the general direction of groundwater flow is from the area of the landfill toward Chestnut Branch, as indicated in Figure 2. Since no aquifer characteristics were available for the immediate site area, no estimate of volumetric flow rates or seepage velocities were made. Site inspection, however, did indicate that the general direction of groundwater flow was probably correct because wide areas of contaminated groundwater seepage were noted along the bank of Chestnut Branch in an area that would be downgradient from the landfill site.

Based on the available information, it appears that the groundwater flow is primarily horizontal in the Cohansey Sands. These sands appear to have a notably higher horizontal hydraulic conductivity than the vertical conductivity of the clayey silts underlying them. Also, if the majority of the contaminant movement was vertical, it is doubtful that the contaminated groundwater seeps along Chestnut Branch would have developed in such an extensive manner.

SITE INVESTIGATIONS

The quantification of groundwater, surface water and contaminant conditions would be done by installation of a series of monitoring wells. These wells should be located so that a maximum amount of information can be gathered at each monitoring point. Further, the wells drilled into the landfill area could possibly encounter drums of hazardous and/or explosive materials. It would be advantageous to have an assessment of the lateral extent of groundwater contamination and the location of buried waste drums prior to installation of monitoring wells. In order to obtain this desired information, a series of geophysical surveys was conducted at the site. The objectives of the surveys were to:

1. locate drums or pockets of waste filled drums within the landfill area, and
2. preliminarily identify the areal extent of contaminated groundwater leaving the landfill site area.

Several geophysical methods were considered for locating the buried drums within the landfill site. Most reports suggested that the barrels were metal and, therefore, very likely to produce magnetic anomalies as well as being good reflectors of energy impulses. Considering these conditions, a metal finder (M-Scope), a portable proton magnetometer, and a subsurface interface radar unit were selected as the types of instruments best suited for the landfill survey. In order to assess the areal extent of contaminated groundwater, it was decided to conduct a subsurface conductivity survey of the site area. A brief description of each instrument's theory of operation will be presented, followed by a discussion of survey results.

Fisher M-Scope

The Fisher M-Scope pipe and cable finder is scientifically designed to detect and accurately locate buried metal pipes, conduits, and miscellaneous metal objects. The equipment detects the presence of metallic objects through the use of an induced electromagnetic field. The object is located and traced by means of this induced field.

The instrument consists of two principal component parts: a directional radio type transmitter and a directional radio type receiver. The function of the transmitter is to generate or induce in the buried metal object the electromagnetic field referred to above. The receiver locates the metal object by detecting and tracing this electromagnetic field.

Proton Magnetometer

The proton precession magnetometer is so named because it utilizes the precession of spinning protons or nuclei of the hydrogen atom in a sample of hydrocarbon fluid to measure the total magnetic intensity. The spinning protons behave as small spinning magnetic dipoles.

These magnets are temporarily aligned or polarized by application of a uniform magnetic field generated by a current within the instrument. When this current is removed, the spin of the protons causes them to precess about the direction of the ambient magnetic field, much as a spinning top precesses about the gravity field. The precessing protons generate a small signal whose frequency is proportional to the total magnetic field intensity.

The intensity of the magnetic field in a specific location is dependent upon several factors, including the presence of metallic objects. The depth of burial of the metals cannot be assessed, but their presence will be reflected by higher magnetic field intensities.

Subsurface Interface Radar

The subsurface interface radar (SIR) is an advanced impulse radar system. The system's transducer is moved along a line while the recorder produces a continuous high resolution profile of the subsurface. A unique feature of the SIR system is its ability to automatically generate a continuous map of subsurface features, not a point-by-point sample from which extrapolations must be made.

During operation, an electromagnetic impulse is propagated into the subsurface soil profile. When the impulse strikes an interface between two materials of differing electrical properties (i.e., a soil bedrock interface, a soil water interface, a metal drum buried in the subsurface, etc.), some of the transmitted impulse energy is reflected and the remainder continues on through the material to other interfaces. The reflected signals are received by the transducer and sent back to the system control unit to be monitored on its oscillograph and printed on a graphic recorder. The graphic record of the signal wave is a close approximation of the interfaces one would see in a vertical wall of a trench dug along the path of the transducer. Metallic drums and pipes produce a unique signature pattern in the recorded data. These signature patterns were used to correlate the results of the subsurface interface radar survey with the proton magnetometer survey. •

Conductivity Meter

The EM34-3 conductivity meter manufactured by Geonics, Inc., is designed to measure subsurface conductivity using an inductive electromagnetic technique. The instrument gives direct readings in millimhos per meter, and surveys are carried out by traversing the ground in a grid pattern with two wire coil units. The principle of operation is that the depth of penetration is independent of terrain conductivity and is determined solely by the instrument geometry, i.e., the intercoil spacing and coil orientation. The instrument can be used at fixed spacings of 10, 20 or 40 meters. The depth of penetration can be stepped from a minimum of 7.5 meters to a maximum of 60.0 meters.

GEOPHYSICAL SURVEY INVESTIGATION RESULTS

The geophysical surveys were conducted in two areas: over the landfill itself, and downgradient from the landfill toward the groundwater discharge point along the bank of Chestnut Branch. Figure 4 shows the areas which were surveyed with each geophysical technique and also indicates which figures show the results of a particular survey. The following paragraphs briefly describe the results obtained with each geophysical technique.

Proton Magnetometer

The landfill site was staked to form a grid having 7.6 meter centers. A magnetometer survey was conducted on this grid spacing, and a contour map portraying the various patterns of magnetic intensity is shown as Figure 5.

The results of the magnetometer survey indicate isolated areas within the landfill where there are anomalously high magnetic values. Buried metallic objects would locally induce these types of magnetometer readings, of which chemical waste drums may be included. The lateral and vertical limits of the magnetic anomalies should not be considered as exact boundaries. The lateral extent is effected by the data point grid spacing. Closer spacing of the grid pattern would more accurately delineate the boundaries of the magnetic highs. The size and/or number of metallic objects and their arrangement would also influence magnetometer values as would the depth of burial and/or the distribution of metallic objects with depth. Therefore, the limits of the suspected areas containing buried metallic objects are approximate, but these limits do represent zones within the landfill that should not be considered for test boring locations.

Subsurface Interface Radar

An SIR survey was conducted on the site during July of 1980. Test runs were made with

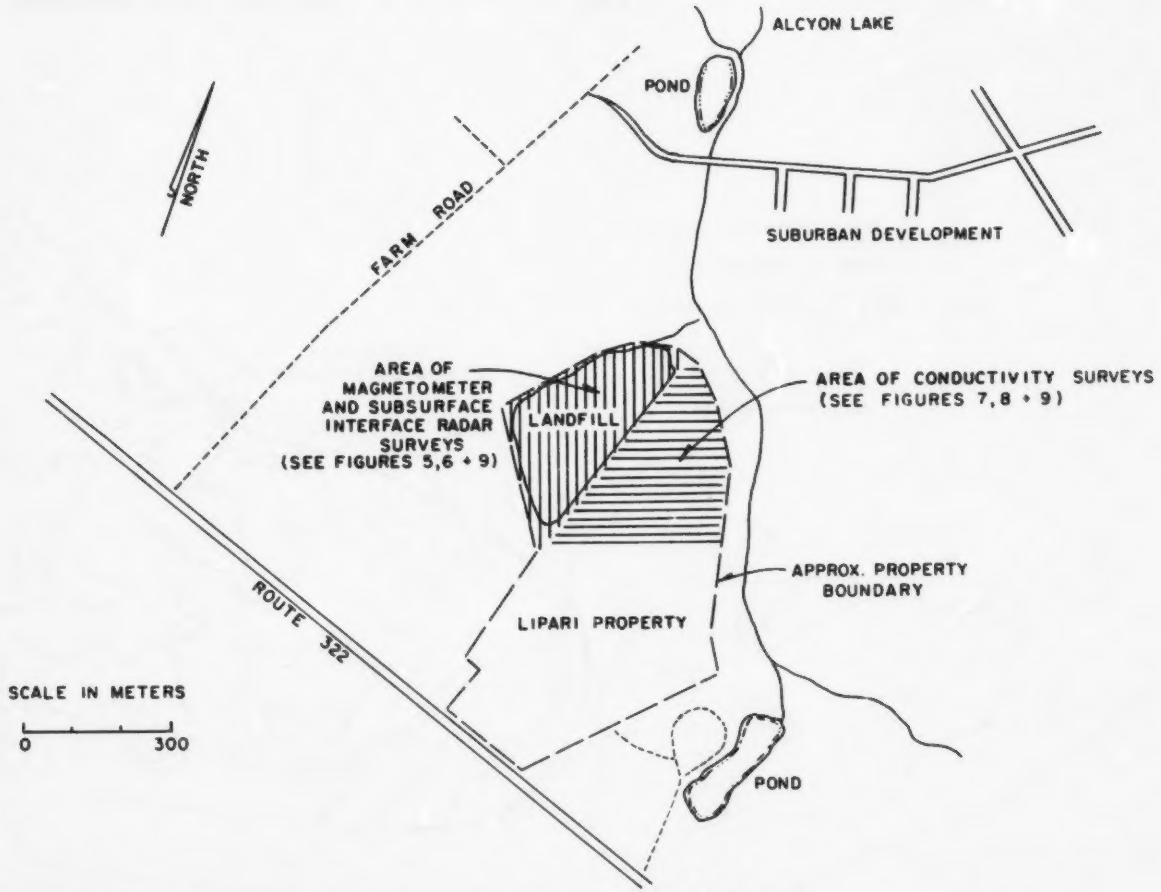

ALCYON LAKE
POND
NORTH
FARM ROAD
SUBURBAN DEVELOPMENT
AREA OF MAGNETOMETER AND SUBSURFACE INTERFACE RADAR SURVEYS (SEE FIGURES 5,6 + 9)
LANDFILL
AREA OF CONDUCTIVITY SURVEYS (SEE FIGURES 7,8 + 9)
APPROX. PROPERTY BOUNDARY
ROUTE 322
LIPARI PROPERTY
SCALE IN METERS
0
300
POND

Figure 4. Geophysical Survey Plan, LiPari Landfill Site Area, Pitman, New Jersey.

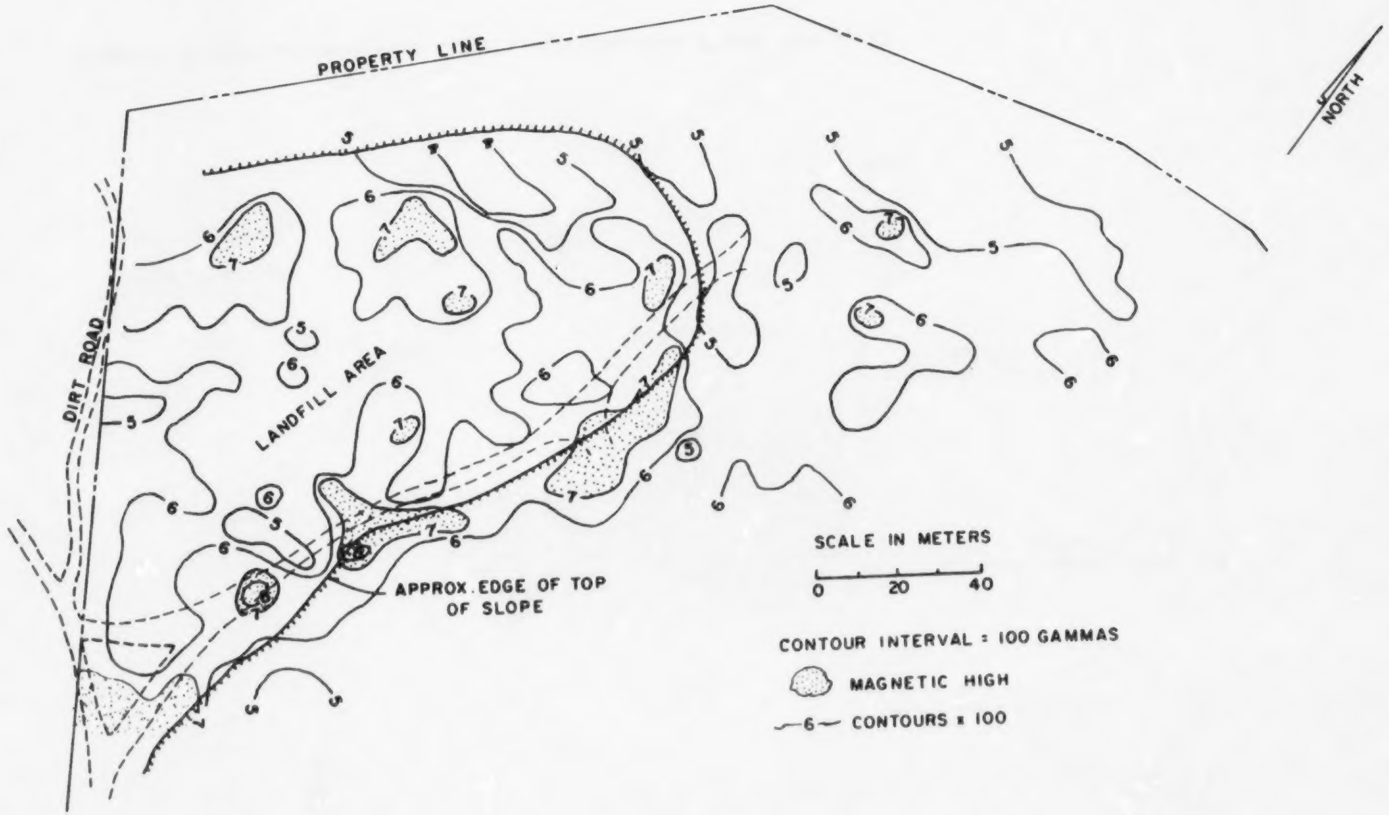

PROPERTY LINE
NORTH
DIRT ROAD
LANDFILL AREA
APPROX. EDGE OF TOP OF SLOPE
SCALE IN METERS
0
20
40
CONTOUR INTERVAL = 100 GAMMAS
MAGNETIC HIGH
6 CONTOURS x 100
5
6
7

Figure 5. Magnetometer Survey, LiPari Landfill Site, Pitman, New Jersey.

various transducers to determine the most practical for the given field conditions. A high resolution transducer was selected. A major portion of the area, along the same 7.6 meter grid lines as used in the magnetometer work, was surveyed. The SIR survey lines are shown in detail in Figure 6 along with a partial listing of the areas where buried metallic objects were detected.

As with the magnetometer survey, the 7.6 meter grid spacing is a factor in determining the number of metallic objects which can be located. The SIR system is more selective than the magnetometer in that only objects directly below the transducer are detected and recorded. The magnetometer measures the magnetic field in the area of the observation point, and a metallic object would not have to be directly below the instrument to have an influence. This difference in measurement techniques must be considered when evaluating and correlating data from each of these instruments. Because of the narrow detection width on the SIR unit, the signatures from metallic drums will probably not appear at the location of each magnetic anomaly. Where drums are seen on the SIR, however, magnetic highs should and in fact did occur. In general, a comparison of the locations of metallic objects determined through the radar survey with the magnetometer survey showed a good association of metallic objects with magnetic highs. Because of the broader area coverage of the magnetometer survey, the magnetic data were considered to be more useful in developing the overall boring location plan within the landfill.

As a check on both of the above methods of investigation, an M-Scope survey was also conducted. This survey was limited to specific areas where both high and low magnetic readings had been obtained. The M-Scope survey results correlated very well with the magnetometer survey results.

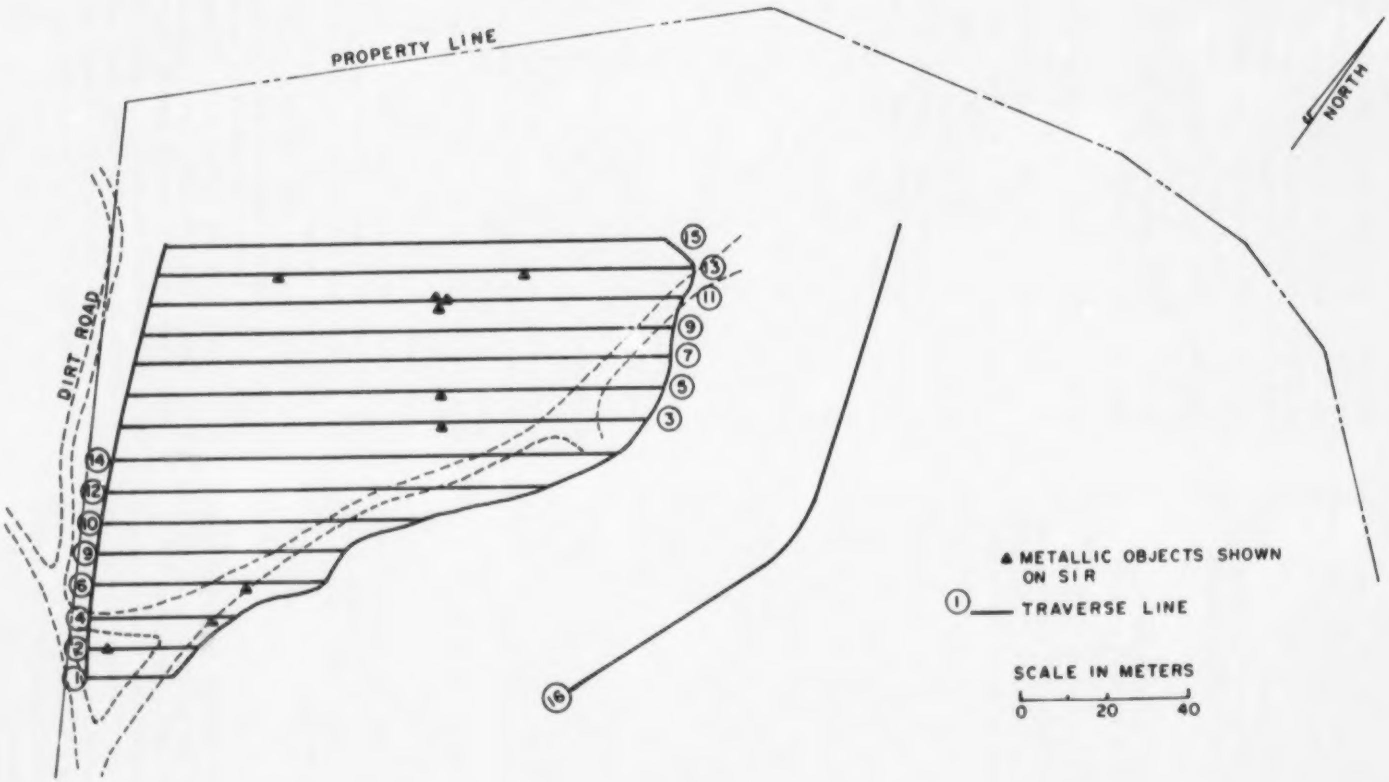
Conductivity Meter

The conductivity survey was conducted over the area east of the landfill, as shown in Figure 4. As discussed above, preliminary field work indicated that groundwater movement was from the landfill toward Chestnut Branch, and thus this site area was selected for the survey. It was considered that contaminants migrating from the landfill would increase the conductivity of the groundwater. This increased conductivity could be measured and plotted, thus providing a preliminary definition of the areal extent of the contaminant plume. The primary survey of the area was run on a grid spacing of 7.6 meters, with an effective investigation depth of 7.5 meters. In order to verify the initial results, a secondary survey was run on a grid spacing of 15.2 meters, with a penetration depth of 15 meters. The results of both surveys were comparable and are shown in contour map form in Figures 7 and 8. It is considered that the conductivity pattern shown in these figures is an approximation of the plume of contaminated groundwater downgradient from the landfill site.

QUALITATIVE ASSESSMENT SUMMARY

The results of the above discussed geophysical surveys and the file information reviewed have provided a basic understanding of the site conditions, at least in a qualitative sense. The approximate locations of metallic wastes within the landfill have been assessed, and the location of the contaminant plume in the groundwater system downgradient of the site has been estimated. A composite map showing the results of both the magnetometer survey and the conductivity survey is provided as Figure 9. These data will be used as the basis for developing the work to be conducted during the quantification phase of the site assessment program.

This work essentially completes the qualitative assessment phase of the site investigation. As can be seen, a significant amount of information has been gathered via geophysical techniques, and these data will facilitate the development of the quantitative phase of work. It should be realized that geophysical techniques have a tremendous potential in the assessment of subsurface conditions in and around landfill sites. It is important, however, that these geophysical applications be made with an understanding of the capabilities and limitations of the specific technique and equipment. As an example, the techniques used in this research study relied heavily on electromagnetic wave propagation. There is very little interference to these types of techniques at the LiPari site. These same techniques may not have been applicable if there were large areas of buried utilities or radio transmission towers in the area. The site conditions must be considered when selecting the types of geophysical surveys or other remote sensing surveys to be conducted.



PROPERTY LINE
NORTH
DIRT ROAD
1
2
4
6
8
10
12
14
3
5
7
9
11
13
15
16
▲ METALLIC OBJECTS SHOWN ON SIR
① TRAVERSE LINE
SCALE IN METERS
0
20
40

Figure 6. Subsurface Interface Radar Survey, LiPari Landfill Site, Pitman, New Jersey.

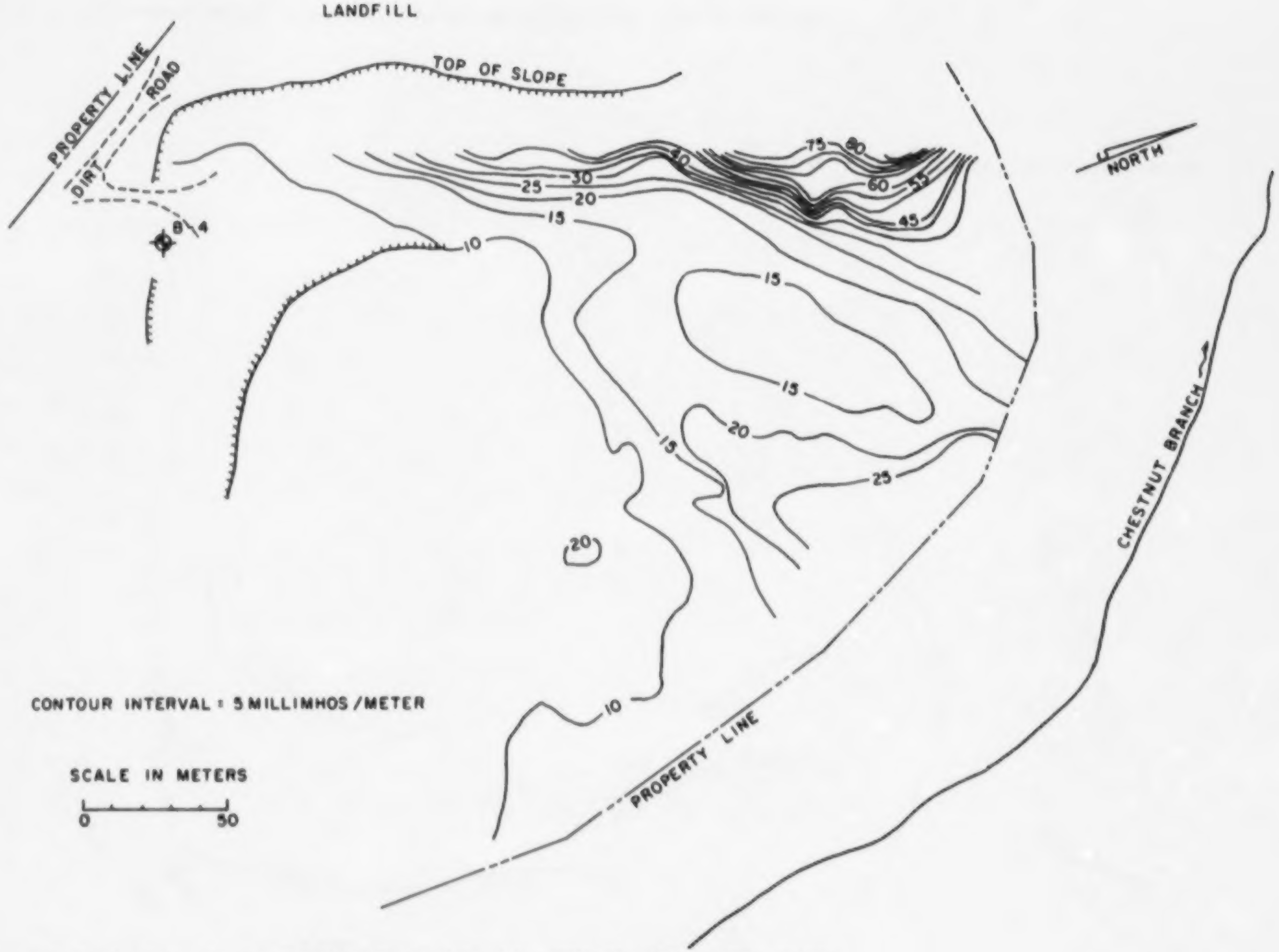

LANDFILL
TOP OF SLOPE
PROPERTY LINE
DIRT ROAD
B 4
NORTH
CHESTNUT BRANCH
PROPERTY LINE
75
80
60
55
45
40
30
25
20
15
10
15
15
20
25
15
20
10
CONTOUR INTERVAL = 5 MILLIMHOS/METER
SCALE IN METERS
0
50

Figure 7. Conductivity Survey, 7.5 Meter Depth, LiPari Landfill Site, Pitman, New Jersey.

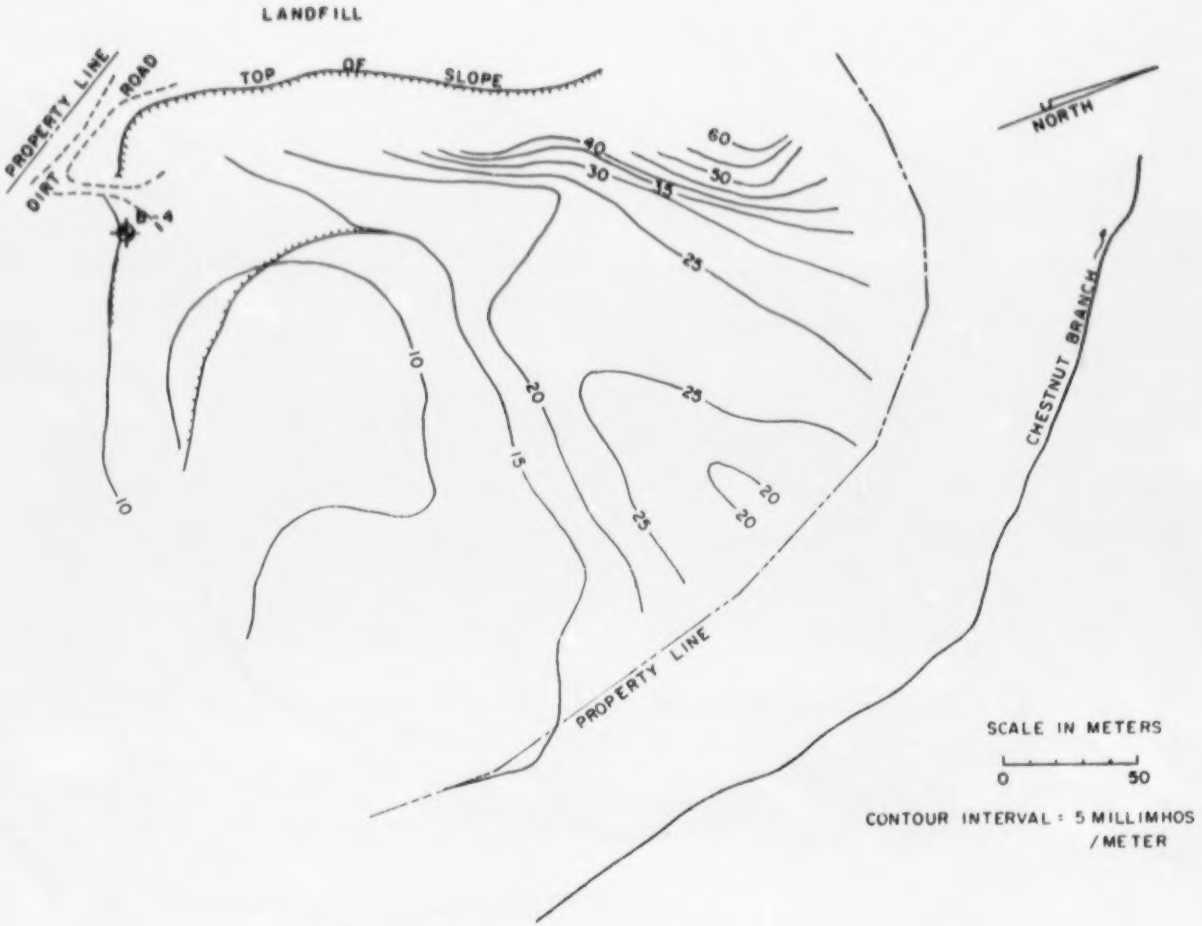

LANDFILL
TOP OF SLOPE
PROPERTY LINE
DIRT ROAD
B-4
NORTH
60
50
40
35
30
25
25
25
25
20
20
20
15
10
10
PROPERTY LINE
CHESTNUT BRANCH
SCALE IN METERS
0
50
CONTOUR INTERVAL : 5 MILLIMHOS /METER

Figure 8. Conductivity Survey, 15.0 Meter Depth, LiPari Landfill Site, Pitman, New Jersey.

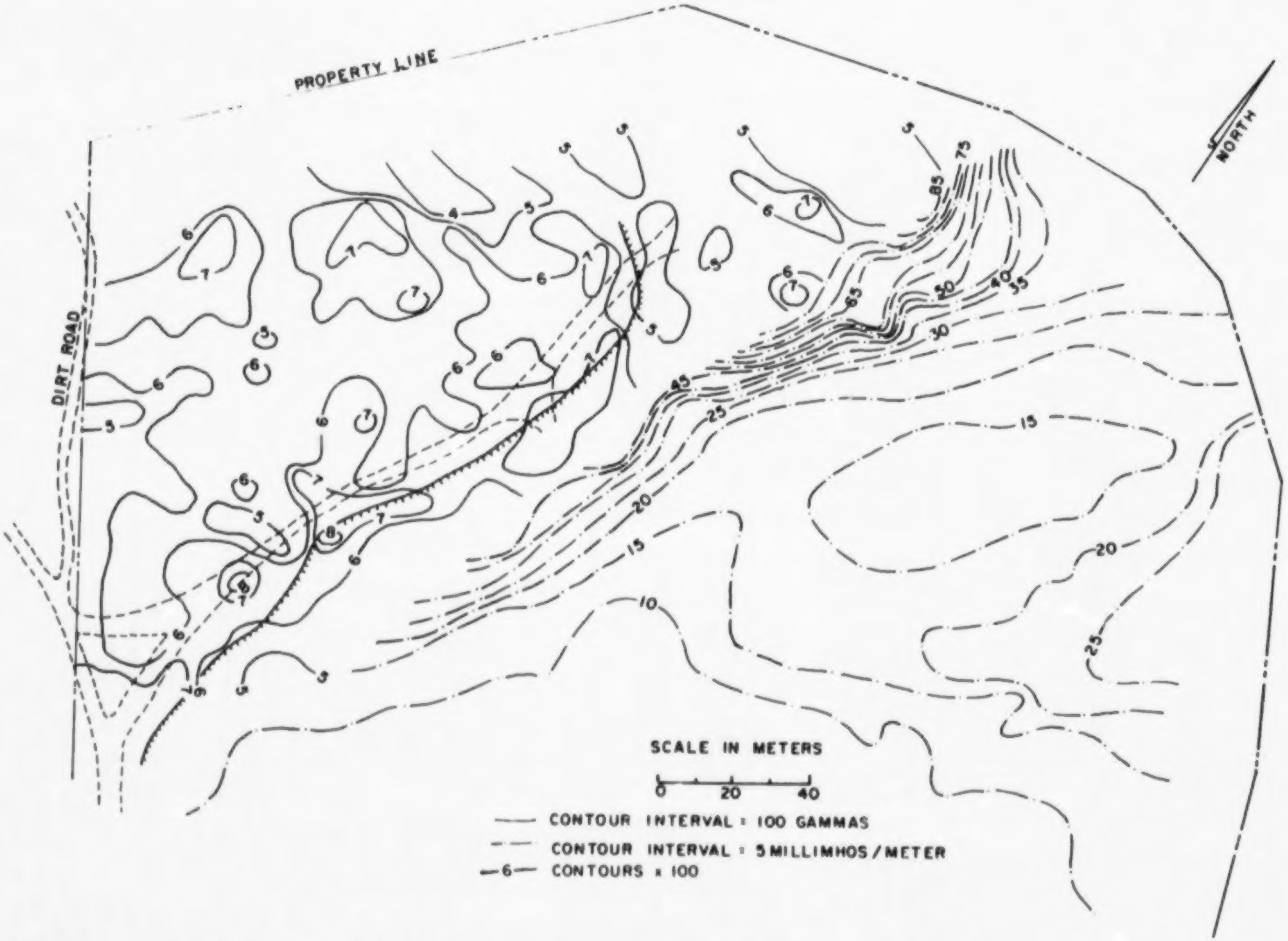

PROPERTY LINE
DIRT ROAD
NORTH
SCALE IN METERS
0
20
40
CONTOUR INTERVAL : 100 GAMMAS
CONTOUR INTERVAL : 5 MILLIMHOS/METER
—6— CONTOURS x 100
5
6
7
8
4
10
15
20
25
30
35
40
45
50
65
75
85

Figure 9. Composite Magnetometer and Conductivity Survey Results, LiPari Landfill Site, Pitman, New Jersey

REMEDIAL ACTIONS AT UNCONTROLLED HAZARDOUS WASTE SITES

Nancy S. Neely, James J. Walsh
Dennis P. Gillespie, and Frederick J. Schauf
SCS Engineers
Covington, Kentucky

ABSTRACT

During the Summer of 1980, a nationwide survey was conducted to determine the status of remedial measures applied at uncontrolled hazardous waste disposal sites. Remedial actions were found to have been implemented at drum storage areas, incinerators, and injection wells, but most frequently at landfills, dumps, and surface impoundments. At the sites receiving such remedial actions, ground water was found to be the most commonly affected media, followed closely by surface water.

Remedial activities encountered usually consisted of containment and/or removal wastes. The survey determined that a lack of sufficient funds and/or improper selection of corrective technologies were responsible for remedial actions having been applied effectively only a portion of the time.

Nine sites were studied in detail to document typical pollution problems and remedial actions at uncontrolled waste sites. Of these, remedial actions were completely effective at only two. Technologies employed at these nine sites represented (1) containment, (2) removal of waste for incineration or secure burial, (3) surface water controls, and/or (4) ground water controls.

INTRODUCTION

Government agencies and private citizens have become increasingly aware of enviornmental problems associated with unsound disposal and transport of hazardous materials. An ABC News-Harris poll, conducted after the headlines of Love Canal, N.Y., and Elizabeth, N.J., found that 76 percent of those surveyed considered the dumping of toxic chemicals to be a serious problem. Ninety-four percent of those interviewed wanted federal standards prohibiting such dumping made stricter than they are now. [1]

The magnitude of hazardous waste problems can be reviewed by examining the quantity of generated waste and the safety of disposing the waste. The U.S. Environmental Protection Agency (EPA) Office of Solid Waste (OSW) estimates that 336 Million metric tons (wet weight) of industrial wastes are produced annually in the United States and that the yearly growth rate is about 3 percent. About 10 percent of this industrial waste is estimated to be potentially hazardous. [2]

Eight EPA regions estimated that 4 percent of all disposal sites (32,000) receiving hazardous waste might pose a significant problem. [3] In contrast, another study [4] estimates that 90 percent of all hazardous waste has been disposed in an unsound manner. A third study [3] conducted for the OSW used both these percentages along with the total number of sites accepting hazardous waste as estimated by the regions and by the report's author to predict the number of sites that might pose significant problems. The total number of sites that contain hazardous waste was thereby calculated to range from 32,000 to 51,000 and the number posing significant problems to range from 1,200 to 34,000.

When one considers the number of sites which could pose significant problems and the number of sites which have already endangered the environment, it is evident that comprehensive programs for enforcement and remedial action response are needed. The Solid and Hazardous Waste Research Division (SHWRD) of EPA's Municipal Environmental Research Laboratory conducts research and development to meet the needs of remedial responses to uncontrolled hazardous waste sites. This research and development program is investigating technologies for the prevention, control, and concentration of hazardous substances released from uncontrolled waste sites. The types of remedial action initiated at uncontrolled sites include more permanent, long-term remedial actions, as well as short-term, emergency responses. EPA SHWRD in Cincinnati, OH is responsible for addressing permanent, long-term responses and the Oil and Hazardous Materials Spills Branch (OHMSB) in Washington, D.C. for emergency, short-term responses. [4]

Several federal laws (i.e., Resource Conservation and Recovery Act, Clean Water Act, Safe Drinking Water Act, and Toxic Substances Control Act) as well as state and common laws provide enforcement provisions which enable the government to attempt to return a polluted or endangered environment to its original state and to force the responsible party to reimburse the government for funds expended. However, the nature of improper disposal of hazardous waste makes proof of liability difficult, since the cause and effect relationship between the act of disposal and eventual harm may not appear for 20 years or more. [5]

To date, the two major laws which have provided federal assistance for remedial action at uncontrolled hazardous waste sites are the Clean Water Act (CWA) and the Resource Conservation and Recovery Act (RCRA). Under Section 311 of the CWA, money is available for emergency remedial action at sites where release of oil or hazardous materials threatens navigable waters. However, land spills that do not directly threaten surface water are not covered under Section 311.

The authorities under CWA and RCRA enable EPA to (1) supply limited assistance for enforcement related investigations (e.g., chemical analysis, site investigation, technical assistance); (2) take emergency remedial action where navigable waters are threatened; and (3) take legal action in cases where sites pose an imminent hazard. Remedial actions at sites where navigable waters are not threatened can only be initiated and funded by states, local governments, and responsible parties. Usually in cases where 311 funds are not used, extensive time is involved in identifying the problem, the responsible party, and the remedial measure which is likely to be successful. Even more time is often required in getting the responsible party to clean up such sites, either voluntarily or through court action. As a result of these conditions, "Superfund" has been proposed to fill the legislative gap described above.

PROJECT DESCRIPTION

In an effort to determine the type and effectiveness of past remedial actions at uncontrolled sites, a nationwide survey of on-going and completed remedial actions projects was conducted from May to October 1980. The purpose of the survey was to provide information and examples of applied remedial action technologies. Examples provided in the form of case histories identify typical problems, effectiveness, and costs related to implementing remedial actions at such facilities.

In identifying remedial action sites, emphasis was placed upon landfill, dump, surface impoundment, drum storage, incinerator, and deep well injection facilities. For the purposes of this survey, a waste burial site was designated as a "landfill" if it was permitted and would include sites resulting from midnight dumping and roadside dumping. Surface impoundments include pits, ponds, and lagoons used for the treatment, storage and/or disposal of wastewater or sludge. Injection wells include subsurface disposal wells and for the purposes of the survey include such sites as abandoned mine shafts. Incinerators included facilities which dispose of wastes by burning.

Case history sites were chosen after consideration of the following factors: (1) legal actions which would hamper an in-depth investigation, (2) the extent and nature of the environmental problem associated with the site; (3) the nature and effectiveness of the applied remedial action; and (4) access to the site and appurtenant file information.

SURVEY FINDINGS AND LITERATURE COMPARISON

Initially 199 sites were identified as having some form of remedial action. Thirty of these sites were later deleted from the list due to either (1) lack of sufficient information, (2) insufficient progress on planned remedial action, or (3) the use of "low-technology" remedial actions. "Low-technology" actions were defined to include measures such as (1) merely filling a lagoon with native soil without instituting surface or ground water controls, (2) discontinuing waste receipts at a landfill without attempting to properly close the facility, or (3) clearing a drum storage facility without regard to existing soil or water contamination.

Various approaches and remedial measures for the cleanup of uncontrolled sites have been published. [4,6] Generally the procedure used in identifying and carrying out the remedial measure to be employed includes the following steps:

- The problem is identified and the site is investigated.
- The problem is assessed. The urgency of applying immediate short term remedial measures is determined. The need for long term actions needed to solve the problem is determined and the source of funding is identified.
- Preliminary design and cost estimates for candidate remdial actions are prepared.
- Remedial actions are implemented with the funds being supplied by the responsible party or other sources.

Table 1 is presented to briefly summarize the standard remedial methods used at an uncontrolled site. The reader is referred to references 4 and 9 for a more complete listing and a description of remedial measures.

TABLE 1. REMEDIAL ACTION TECHNIQUES [4]

Surface Water Controls
- Grading Operations
- Revegetation
- Surface Water Diversion
- Surface Water Collection

Groundwater Controls
- Impermeable Barriers
- Permeable Treatment Beds
- Groundwater Pumping
- Bioreclamation
- Contaminated Water Treatment
- Plume Containment

Leachate Control
- Subsurface Drains
- Drainage Ditches
- Liners
- Leachate Recycle

Gas Migration Control
- Pipe Vents
- Trench Vents
- Gas Barriers
- Gas Collection Systems
- Gas Treatment Systesm
- Gas Recovery

Direct Waste Treatment
- Excavation
- Hydraulic Dredging
- Land Disposal
- Incineration
- Solidification
- Encapsulation
- In-Situ Treatment
- Wet Air Oxidation
- Neutralization/Detoxification
- Microbial Degration

Treatment of Contaminated Sewer and Water Lines
- In-Situ Cleaning
- Leak Detection and Repairs
- Removal and Replacement
- Chemical Treatment

Contaminated Sediments
- Mechanical Dredging
- Low Turbidity Hydraulic Dredging
- Dredge Spoil Management
- Revegetation
- Physical/Chemical Treatment

The survey of 169 remedial action sites revealed that a variety of remedial measures included containment on-site, chemical/physical treatment (neutralization of acids and bases, precipitation, etc.), biological treatment (land spreading, oxidation ponds, and underground enhancement of native microbes using fertilizer), incineration, and removal and burial in a secure landfill. The remedial measure most often employed consisted of containment and/or removal of the hazardous waste. Cost was found to be the prime determinant of the type of technology applied. As a result, the primary remedial goal has been prevention of further contamination of the environment rather than complete cleanup. Complete cleanup can require millions of dollars, sophisticated technologies, and long periods of time.

When hazardous material was contained in its original location, surface water controls were generally constructed (e.g., grading, diversion ditches, revegetation, surface sealing, etc.) In most instances where the ground water was contaminated, a major portion of the waste was removed and sent to a secure landfill or incinerated and surface water controls were constructed to secure the remaining contaminants. Implementation of controls for ground water cleanup is typically more expensive and time-consuming than implementation of surface water controls. Accordingly, ground water remedial measures were implemented at only a few sites. Ground water pumping was the most often applied such control while remedial measures such as bentonite slurry trenches or sheet pile cutoff walls were found at some spill sites.

Tables 2 through 5 were compiled based upon information gathered during the survey. Over 130 individuals were contacted to compile the data. Some of the factors which should be considered in reviewing the data present in the following survey tables include: (1) the data was based solely upon the immediate survey findings, as reported by individuals contacted; (2) a "potential" threat was not considered sufficient for the site to be included in the inventory; while (3) a probable (but undocumented) contamination was taken as a positive finding.

Table 2 indicates the types of disposal facilities experiencing remedial actions. It should be noted that the total number of facilities (204) shown in Table 2 does not coincide with the number of identified sites (169). The higher number is the result of different types of facilities being located on the same property. More surface impoundments and landfills were identified as experiencing remedial action than other types of disposal facilities. This would be anticipated since surface impoundments and landfills are the most prevalent types of disposal method.

TABLE 2. FACILITY TYPE AT REMEDIAL ACTION SITES

Facility Type	Number of Sites		
	Status		Total Number
	Active	Inactive	
Landfill	16	37	53
Dump	0	27	27
Drum Storage	11	25	36
Surface Impoundment	18	37	55
Injection Well	1	3	4
Incinerator	1	5	6
Spill	0	23	23
Total			204

Table 3 was compiled to determine the geographical location of sites which had undergone remedial action. During conversations with federal officials, it became apparent that many factors affect the geographical distribution. For example, industrial waste disposal sites would typically predominate in those states which have more industry. The possibility of a large number of uncontrolled sites needing remedial measures would increase with an increase in the number of industrial disposal sites. However, the presence of more uncontrolled sites needing remedial measures did not necessarily mean remedial measures were being applied. Institution of remedial measures is dependent upon time and force exerted by public officials, as well as the environmental concern of the site's owner/operator. In order to provide a perspective of remedial action sites, U.S. total waste sites, the third column in Table 3 demonstrates the number of high-risk hazardous waste sites which still require clean-up activities.

TABLE 3. LOCATION OF REMEDIAL ACTION VS. UNCONTROLLED WASTE SITES

State	Remedial Action Sites*	High-Risk Uncontrolled Waste Sites+
Alabama	2	11
Alaska	0	0
Arizona	3	0
Arkansas	2	1
California	3	2
Colorado	3	12
Connecticut	4	2
Delaware	2	0
Florida	7	3
Georgia	4	0
Hawaii	0	0
Idaho	0	0
Illinois	8	0
Indiana	3	1
Iowa	1	1
Kansas	2	0
Kentucky	5	3
Louisiana	3	3
Maine	2	0
Maryland	1	4
Massachusetts	5	3
Michigan	11	5
Minnesota	3	7
Mississippi	0	1
Missouri	4	0
Montana	5	2
Nebraska	0	0
Nevada	0	0
New Hampshire	1	3
New Jersey	10	8
New Mexico	0	1
New York	14	5
North Carolina	7	5
North Dakota	6	0
Ohio	4	2
Oklahoma	0	0
Oregon	0	3
Pennsylvania	16	21
Rhode Island	4	2
South Carolina	3	3
South Dakota	0	0
Tennessee	10	2
Texas	3	1
Utah	1	0
Vermont	0	0
Virginia	2	1
Washington	0	2
West Virginia	1	0
Wisconsin	3	0
Wyoming	1	0
Total 50 States	169	120

*As determined by this survey

+From reference 1.

Public awareness and environmental consciousness were strong factors in implementation of remedial measures. Pressure exerted by state officials sometimes forced companies and property owners to implement corrective actions. Since remedial action is generally a time-consuming endeavor, the number of remedial action sites was also dependent upon how long ago the environmental concerns were emphasized. Legal action to identify "responsible" persons for remedial actions generally took four to nine years. After this time, the identified responsible party either instituted remedial actions at the site or declared bankruptcy (in the process refusing to remedy the situation).

A study conducted on 421 cases associated with land disposal of industrial and pesticide waste damage revealed that the ground water was affected 65 percent of the time and the surface water was affected 40 percent of the time. [6] According to Table 4 ground water and surface water were the most often affected media at the 160 remedial action sites. Ground water was affected 65 percent of the time; surface water, 56 percent; soil, 41 percent; air, 29 percent; and food chain, 12 percent of the time. Frequently a site affected more than one media.

TABLE 4. AFFECTED MEDIA AT 169 REMEDIAL ACTION SITES

Affected Media	Number of Occurences
Ground Water	110
Surface Water	95
Air	49
Soil	69
Food Chain	20
Total	343

Generally the state, county, and/or municipality attempted to persuade the owner/operator of an uncontrolled facility to voluntarily remedy the environmental hazards. If this effort failed, legal proceedings were instituted against the responsible party. Depending on the degree of hazard posed by the site, various government agencies funded the remedial activities while legal responsibility was determined by the courts. Federal financial assistance for remedial measures was usually found to be funded under Section 311 of CWA. As previously stated, these funds are available only for endangerment of navigable waters. Since any one site might require millions of dollars, total funding from state, county, or municipal sources was unlikely. As a result of these high costs, more than one party often funded remedial activities.

Table 5 was compiled to determine the general status of improvement that occurred at sites which had undergone remedial actions. A total of 180 separate remedial action efforts were initiated at the 169 sites. The pollution status was considered to be "unimproved" when the implemented remedial measure did not correct the contamination problem. Usually lack of improvement was the result of inadequate funds or the type of action instituted. Improved refers to a remedial measure which may have partly corrected the problem, but some problems are still experienced at the site. A remedied site was one at which the problem had been corrected; e.g., contaminated surface water was returned to its natural state. Based on these definitions, the last column in Table 5 indicates that 46 percent of corrective actions were not effective, 38 percent improved the pollution problem, and 16 percent were completely effective.

TABLE 5. POLLUTION AND REMEDIAL ACTION STATUS AT 169 SITES

	Number of Remedial Actions			
Pollution Status	Planned Actions	On-Going Actions	Completed Actions	Total
Unimproved	16	49	17	82
Improved	12	36	21	69
Remedied	0	3	26	29
Total	28	88	64	180*

* A total of 180 remedial activities were identified at the 169 sites.

CASE STUDY FINDINGS

Case study sites were selected based on a desire to represent a range of facilities, pollution, and remedial actions. Tables 6, 7, and 8 present an overview of the nine case histories. The nine sites include two remedied and seven improved sites. Remedial action applied at the seven improved sites showed varying degrees of effectiveness. The combination of all nine sites covered contamination of all media including ground water, surface water, soil, air, and the food chain.

Waste types involved included mercury, arsenci, solvents, oil, tire wastes, inorganic and organic waste, and septic waste. The types of facilities examined included surface impoundments, landfills, drum storages, and incinerators. The technology employed consisted mainly of containment, removal of waste for incineration or secure burial, and institution of surface water and/or ground water controls. Costs for implemented remedial actions ranged from $250,000 to more than $7,000,000.

TABLE 6. CASE STUDY SITE IDENTIFICATION

Site No.	Name	Location	Waste Type	Remedial Action Technology
A	Olin Corporation	Saltville, PA	Mercury	Graded and constructed erosion conrol structures. Removed contaminants. Planning extensive remedial action ($23 million).
B	Firestone Tire and Rubber	Pottstown, PA	Tires, SO_2 scrubber waste, organic waste, pigments, PVC sludge	Recovery wells intercepted polluted ground water and recycled it through their plant. Expected to be 100 percent effective.
C	Anonymous	East Central, NY	Solvents, oils, paint waste with PCB	Lagoons filled and capped. Diversion ditches and test wells installed.
D	Destructo/Carolawn	Kernersville, NC	Volatile/flammable waste	Two Phases: 1. Waste removed, incinerated or landfilled. Contaminated soil removed and landfilled. 2. Waste removed, incinerated, landfilled, and deep well injected.
E	Whitmoyer Laboratories	Myerstown, PA	Arsenic compounds	Removed arsenic waste from lagoon, treated and discharged. Waste piles of arsenic placed in concrete vault. Ground water treated using purging wells. Some contaminated soil remains.
F	Western Sand and Gravel	Burrillville, RI	Septic plus hazardous wastes	Four lagoons pumped, dried, and contents stored off and on-site. Monitoring wells installed. Future remedial action planned.
G	Ferguson Property	Rock Hill, SC	Solvents, heavy metals	Two Phases: 1. Contained with polyethylene and clay cap. Installed surface water diversion ditches and vent pipes in contained area. 2. Since phase one ineffective, removed liquid. Still some sludge and drums left.
H	3M Company	Woodbury, MN	Spent solvents, acid sludge	Pits emptied and contents burned. Barrier wells installed to stop spread of contaminated ground water.
I	Whitehouse/Allied Petroleum	Jacksonville, FL	Oil, PCB	Mobile activated carbon unit dewatered pit, oil absorbed using solid waste and earth. Future remedial action planned.

TABLE 7. CASE STUDY SITE BACKGROUND

										Pollution								Remedial Action										
	Facility Type							Status		Affected Media					Status			Funding					Status			Litigation		
Site No.	Landfill	Illegal Dump	Drum Storage	Surface Impoundment	Injection Well	Incineration	Spill	Active	Inactive	Ground Water	Surface Water	Air	Soil	Food Chain	Remedied	Unimproved	Improved	Federal	State	County	Municipal	Private	Completed	On-Going	Planned	Current	No	Expected
A	x			x					x	x	x		x				x					x	x		x		x	
B	x			x				x		x	x		x		x							x		x			x	
C	x			x					x	x	x	x	x	x			x					x	x		x		x	
D			x			x	x		x		x	x		x			x	x					x			x		
E	x			x					x	x	x		x				x					x	x				x	
F				x					x	x	x	x	x				x	x	x					x	x		x	
G			x						x				x				x	x					x	x		x		
H				x					x	x					x							x		x			x	
I				x			x		x	x	x		x	x			x	x	x		x		x	x	x		x	

TABLE 8. REMEDIAL ACTION COSTS AT CASE STUDY SITES

Site No.	Waste Type	Remedial Action				Estimated Cost
		Surface Water Controls	Ground Water Controls	Direct Waste Treatment	Contaminated Water Treatment	
A	Mercury	x				$ 400,000
B	Tires, SO_2 Scrubber Waste, Organic Waste Pigments, PUC Sludge		x			250,000
C	Solvents, Oils, Paint Waste with PCB	x				Unknown
D	Volatile/Flammable Waste			x		> 364,000
E	Arsenic Compounds		x	x	x	Unknown
F	Septic plus Hazardous Wastes			x		>1,000,000*
G	Solvents, Heavy Metals	x		x		143,178
H	Spent Solvents, Acid Sludge		x	x		> 7,000,000
I	Oil, PCB			x	x	> 253,000*

*Estimated

CONCLUSION

Remedial measures encountered during this survey were usually confined to containment and/or removal of the hazardous wastes. The primary goal was to prevent further contamination of the environment rather than to perform a complete cleanup. Complete environmental cleanup of ground water or surface water generally requires sophisticated technology, additional money, and additional time. Therefore, a responsible party with sufficient funds and expertise must be located before complete cleanup can occur. In most cases sufficient funds have not been available for effective remedial action. The U.S. EPA is able to provide only limited funds under Section 311 of the CWA. States and local governments typically cannot provide sufficient money for total cleanup, since correction of one site may require millions of dollars.

Based on the case studies and survey, the state-of-the-practice in remedial action does not look favorable. Fully 46 percent of the time the applied remedial action was ineffective and only a portion of all uncontrolled sites have received some form of remedial action. Remedial action applied at a site experiencing problems was found to be totally effective only 16 percent of the time.

It should be emphasized that the numbers presented in this section are based on assumptions by the persons performing the survey and the opinions of those interviewed. However, the percentage numbers should be a fairly accurate representation of the state-of-the-practice in remedial actions.

REFERENCES

1. Magnuson, Ed, et al. 1980. The Poisoning of America. TIME, Sept.22, 1980, pp.58-69.

2. Metry, Amer A., 1980. Comprehensive Hazardous Waste Management. In the Handbook of Waste Management. Technomic Publishing Co., Inc., Westport, Connecticut, pp. 45-89.

3. Fred C. Hart Associates, Inc., 1979. Preliminary Assessment of Clean Up Cost for National Hazardous Waste Problems. Prepared for the Office of Solid Waste, Contract #68-01-5063.

4. Hill, Ronald D., et al. 1980. USEPA Research Program: Uncontrolled Hazardous Waste Sites. In Proceedings of National Conference on Management of Uncontrolled Hazardous Waste Sites, U.S. Environmental

Protection Agency, Washington, D.C., pp. 173-179.

5. Brandwein, David I., 1980. The Dimensions of Corporate Liability. In Proceedings of National Conference on Management of Uncontrolled Hazardous Waste Sites, U.S. Environmental Protection Agency, Washington, D.C., pp. 262-268.

6. Ghassemi, Masood, et al. 1980. Comparative Evaluation of Processes for the Treatment of Concentrated Wastewaters at Uncontrolled Hazardous Waste Sites. In Proceedings of National Conference on Management of Uncontrolled Hazardous Waste Sites, U.S. Environmental Protection Agency, Washington, D.C., pp. 160-164.

7. Paige, Sidney, et al. 1980. Preliminary Design and Cost Estimates for Remedial Actions at Hazardous Waste Disposal Sites. In Proceedings of National Conference on Management of Uncontrolled Hazardous Waste Sites, U.S. Environmental Protection Agency, Washington, D.C., pp. 202-207.

8. Pease, Robert A. Jr., et al. 1980. Management of Abandoned Site Cleanups: Wade Property, Chester, Pennsylvania. In Proceedings of National Conference on Management of Uncontrolled Hazardous Waste Sites, U.S. Environmental Protection Agency, Washington, D.C., pp. 147-151.

9. Sills, Michael A., et al. 1980. Evaluation of Remedial Treatment, Detoxification and Stabilization Alternatives. In Proceedings of National Conference on Management of Uncontrolled Hazardous Waste Sites, U.S. Environmental Protection Agency, Washington, D.C., pp. 192-201.

BARREL AND DRUM RECONDITIONING
INDUSTRY STATUS PROFILE

C. J. Touhill
Touhill, Shuckrow and Associates, Inc.
Pittsburgh, Pennsylvania 15237

Stephen C. James
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

ABSTRACT

This report is an industry profile of drum reconditioning process characteristics and the current status of pollutant generation and disposal. An overview of the reconditioning industry describes number, location, and types of facilities, and estimates the volumes of drums processed. Drum characteristics, new drum production, and users are defined. Washing and burning processes for reconditioning are described along with operating and design criteria for individual unit operations. The descriptions define typical industry practice. Processing procedures which influence product quality and environmental pollutant generation are discussed. Processing of pesticide containers is discussed especially with regard to the ability of reconditioning procedures to detoxify pesticide residuals. Pollutant loadings are defined in terms of sources and pathways, major pollutant parameters, and generation and disposition modes. Discharge data is given for wastewater discharges and residues. Current status of pollution control practice is defined in terms of processes and equipment, operating procedures, disposal practices, removal efficiencies, and costs.

Introduction

For many people, the spent 208 liter (55-gallon) steel drum has become the symbol of toxic and hazardous wastes. Even though drum reconditioning is intended to support environmentally desirable goals of recycle, reuse, and safe disposal of used drums, popular equating of drums and hazards focuses adverse attention upon the industry. The Environmental Protection Agency (EPA) recognizes the useful service performed by reconditioners, but also is alert to potential problems the industry may encounter in meeting high standards of environmental quality. Because of this awareness, EPA contracted with the firm of Touhill, Shuckrow and Associates, Inc. (TSA) for the following purposes:

- to define representative practice for barrel and drum reconditioning by washing and burning
- to determine the environmental impact of reconditioning processes
- to recommend procedures for designing, optimizing, and retrofitting reconditioning facilities to meet rigorous environmental standards
- to determine the capabilities of the reconditioning industry to process pesticide and toxic chemical containers safely.

The TSA project is being conducted in three parts. In the first, current status of the industry is evaluated in terms of state-of-the-art practices for both reconditioning and pollution control. Results of this evaluation are the subject of this paper. In the second part of the program, which will be reported upon separately, three reconditioning sites were selected for sampling and analysis to define more closely pollutant sources and pathways. The final phase will be development of recommendations for design modifications, process optimization, and retrofitting reconditioning processes.

Five sources of information were used to prepare the first phase report: 1) publicly available literature, 2) transcripts of National Barrel and Drum Association (NABADA) forums on reconditioning problems and techniques, 3) proceedings of four International Conferences on Steel Drums, 4) responses to a questionnaire sent by NABADA to its membership, and 5) visits to eleven drum reconditioning plants.

Industry Overview

During 1979, about 250 reconditioners processed more than 41 million steel drums. More than 95 percent were 208 liter (55-gallon) drums; most of the rest were 114 liters (30-gallons). About two-thirds of the drums are reconditioned at washing plants which process tight head drums. The remainder, open head drums, are burned in drum reclamation furnaces. Facilities that only wash drums account for 39 percent of reconditioning plants. Those that only burn account for 18 percent, whereas 43 percent of the facilities perform both functions.

NABADA members represent only 48 percent of the reconditioning plants in the country, but they process more than 90 percent of all washed drums and more than 97 percent of those burned. For non-NABADA reconditioning facilities, 70 percent recondition for service and resale, and 30 percent are users who process only their own drums. More than half (52 percent) of the drums washed are on a service or laundry basis; 45 percent are for resale. By comparison, only about one-third of drums burned are on a service basis; 62 percent are resold.

In 1972, the U.S. Department of Commerce (1) determined that the reconditioning industry had sales of nearly $110 million (Table 1). This would be more than $210 million in current dollars. At that time, more than 56 percent of the sales were in the Middle Atlantic and Great Lakes states. Based upon present reconditioning volumes and productivity rates (assumed to be 20 drums/day/employee), industry employment is about 7,900. The industry presently is operating at approximately 70 percent of design capacity. The average plant has an 18½ day inventory, most of which is stored on-site.

For many years, the annual ratio of new drums produced to reconditioned has been nearly 1 to 1. Additionally, the ratio of new tight to open head drums (4 to 1) has not changed over the past 10 to 12 years. However, trends show a decrease in drum thickness. For example, in 1969, 18-gage or heavier drums comprised 64.3 percent of those manufactured that year. In March of 1980, that percentage had fallen to 41.4. This reduces the pool of potentially reconditionable drums, because thinner drums are less able to withstand the rigors of transportation and reconditioning processes.

Table 2 shows new and reconditioned drum usage according to three sources. New drum end use is based upon data in the Bureau of Census, Current Industrial Reports on steel shipping barrels, drums, and pails (also known as the M34K reports)(2). Reconditioned usage is based upon data from the 1973 Checchi Report for NABADA (3), and the recent NABADA survey made in conjunction with this project. A high percentage of oil and petroleum drums are used and recycled. On the other

TABLE 1. RECONDITIONER SALES BY REGION (1) (1972 DOLLARS)

REGION	NUMBER OF RECONDITIONERS	SALES (in thousands)
New England	15	5,085
Boston SMSA	6	1,384
Middle Atlantic	86	32,863
New York SMSA	18	6,969
Newark SMSA	13	9,023
Philadelphia SMSA	16	7,248
East North Central	66	28,535
Cleveland SMSA	12	3,035
Detroit SMSA	5	1,708
Chicago SMSA	18	8,521
West North Central	11	2,821
South Atlantic	22	14,940
East South Central	3	280
West South Central	21	7,453
Houston SMSA	4	1,401
Dallas-Ft. Worth SMSA	6	2,019
Mountain	7	1,503
Pacific	32	16,457
Los Angeles SMSA	11	4,729
San Francisco SMSA	6	3,895
TOTAL	263	109,937

TABLE 2. NEW AND RECONDITIONED DRUM USAGE

USE	NEW DRUM END USE (1979) (%)	SHIPPERS TO RECONDITIONERS (%)	
		Checchi	NABADA
Food	5.1	-	6.8
Oil & Petroleum	15.2	37.8	36.2
Paint	6.6	19.0	10.0
Ink		-	4.8
Adhesive	-	9.6	6.8
Resins	-	-	8.8
Industrial Chemicals	40.2	14.1	15.6
Pesticides	-	2.9	0.5
Cleaning Solvents	-	11.3	8.8
Janitorial Supplies	3.1	-	-
Other	9.8	5.3	1.8
Unspecified	20.1	-	-

hand, a low percentage of chemical drums are reused. Hence, it is not surprising that drums containing spent industrial chemicals or chemical residuals comprise a significant number of drums found at abandoned hazardous waste disposal sites, because such drums exit the user system quicker.

Reconditioning Processes

Steel drums are processed by either washing or burning. Because tight head drums almost always are washed, reconditioners frequently refer to washing facilities as tight head plants. Conversely, open head drums are processed almost exclusively by burning; hence burning operations often are called open head plants.

Washing Process

Most drum washing is done with strong hot caustic solution. Despite common usage of this technique, no two tight head reconditioning plants are the same. Certainly there are many similarities, but for maintenance or enhancement of environmental quality standards each plant must be evaluated separately. Nevertheless, a flow diagram which generally represents the caustic washing process and its many variations is shown in Figure 1.

In a washing plant, the following operations generally are employed. After screening and draining upon receipt, drums are preflushed using a strong hot caustic solution. Subsequently, they proceed to a submerged caustic washing tank. When drum contents are difficult to remove using caustic alone, chains are inserted into the drum along with caustic and the drum is tumbled to dislodge adhering materials. If drum contents cannot be removed by chaining or are cleaned only with great difficulty, the drum heads are cut off, thus converting them to open heads, and they are sent to a burning plant. About one-third of washing plants remove rust using hydrochloric acid washes. Tight head drums then are rinsed, dedented, shot blasted, leak tested, and painted.

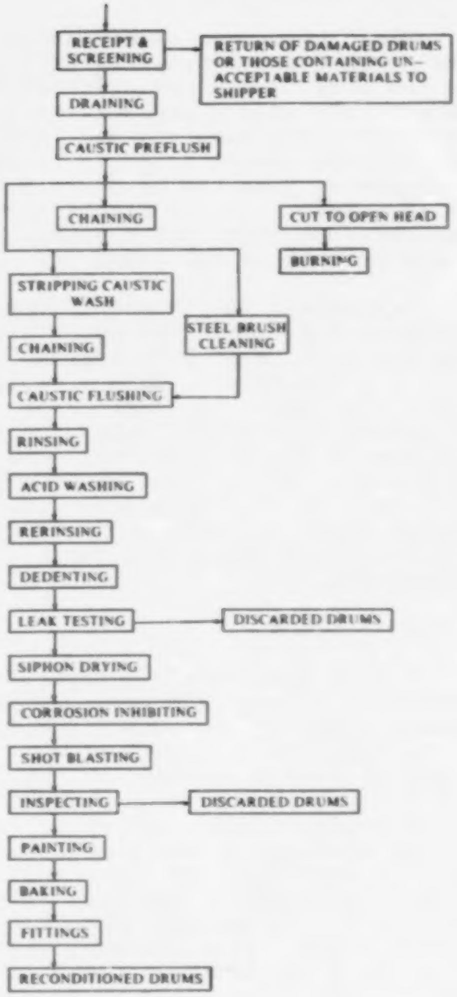

RECEIPT & SCREENING
RETURN OF DAMAGED DRUMS OR THOSE CONTAINING UN-ACCEPTABLE MATERIALS TO SHIPPER
DRAINING
CAUSTIC PREFLUSH
CHAINING
CUT TO OPEN HEAD
BURNING
STRIPPING CAUSTIC WASH
STEEL BRUSH CLEANING
CHAINING
CAUSTIC FLUSHING
RINSING
ACID WASHING
RERINSING
DEDENTING
LEAK TESTING
DISCARDED DRUMS
SIPHON DRYING
CORROSION INHIBITING
SHOT BLASTING
INSPECTING
DISCARDED DRUMS
PAINTING
BAKING
FITTINGS
RECONDITIONED DRUMS

FIGURE 1

WASHING FLOW DIAGRAM

Some operating data derived from the recent NABADA survey are given below. Caustic concentrations averaged 12.2 percent for preflushing and 13.4 percent for submerger or stripper solutions. Temperatures averaged 82°C (180°F) and 84°C (184°F) for preflush and stripper solutions, respectively. Nearly 88 percent of all washing plants chain some drums. Of these, 22 percent chain all drums received. About 38 percent of washing plants use 20° Baume hydrochloric acid washes to remove rust.

Tight head drum dedenting is done at an average pressure of 3.11 kPa (65 psi). Most reconditioners (60 percent) used a pressure of 0.34 kPa (7 psi) for leak testing; however, others choose slightly higher pressures so that the mean was 0.38 kPa (8.0 psi). In the NABADA survey, drum rates through shot blasters ranged from 50 to 450 drums/hr.

Responders to the NABADA questionnaire indicated that water use rate per durm is 66 liters/drum (17.5 gallons/drum). This is for plants that wash, burn, or both. For plants that washed only, the use rate was 50 liters/drum (13.3 gallons/drum). Plants that only burned had a rate of 41 liters/drum (10.9 gallons/drum). Those that perform both functions had a considerably higher rate.

Burning Process

A flow diagram for a typical continuous tunnel drum reclamation furnace operation is shown in Figure 2. In addition, Figure 3 is a sketch of such an operation. At most burning plants, drums are inspected upon receipt, and those containing residues beyond plant criterion for emptiness and those containing unacceptable materials are returned to the shipper along with damaged drums. Some reconditioners drain the drums before burning in order to reduce temperature excursions due to materials in the drum. Others believe that the best way to get rid of the residuals in the drum is to burn them directly; thus, draining before burning is avoided.

Some furnaces have water sprays or steam injection at the inlet opening to prevent flashbacks and possible operator injury. Others have built-in distance barriers to reduce operator exposure to flashbacks.

Conveyor belts move drums through the furnace at an average rate of from 6 to 8 per minute. Average residence time is 6.6 minutes. Mean furnace temperature is 675°C (1250°F), whereas the range encountered in the NABADA survey was 315°C (600°F) to 980°C (1800°F). All drum reclamation furnaces use afterburners to control air emissions. Afterburners are on all the time at more than 80 percent of burning plants. Afterburners operate 95 percent of the time considering an average of all plants. Average temperature and residence time for afterburners is 810°C (1490°F) and 0.5 second. The State of California requires reconditioners who burn pesticide drums to operate afterburners at 900°C (1650°F) using a 0.5 second residence time.

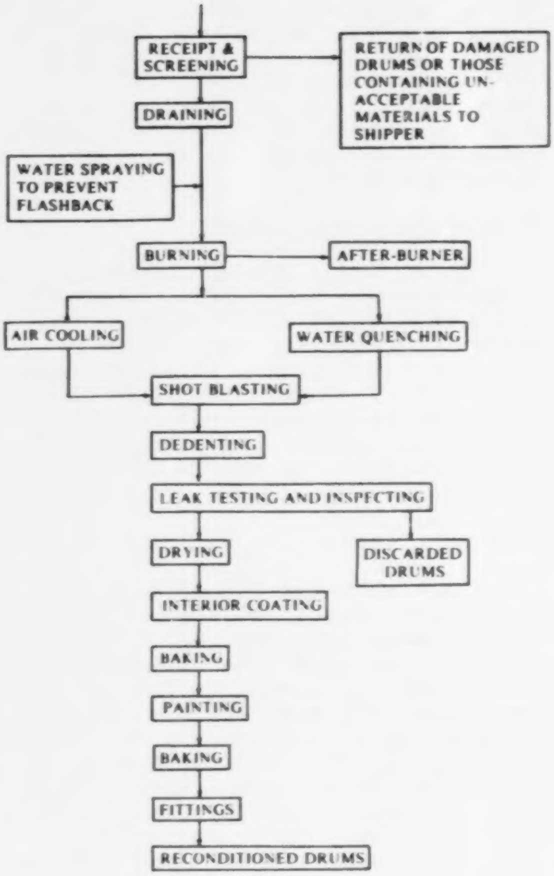

RECEIPT & SCREENING
RETURN OF DAMAGED DRUMS OR THOSE CONTAINING UNACCEPTABLE MATERIALS TO SHIPPER
DRAINING
WATER SPRAYING TO PREVENT FLASHBACK
BURNING
AFTER-BURNER
AIR COOLING
WATER QUENCHING
SHOT BLASTING
DEDENTING
LEAK TESTING AND INSPECTING
DRYING
DISCARDED DRUMS
INTERIOR COATING
BAKING
PAINTING
BAKING
FITTINGS
RECONDITIONED DRUMS

FIGURE 2

BURNING FLOW DIAGRAM

When drums exit the furnace, they are either air-cooled or are

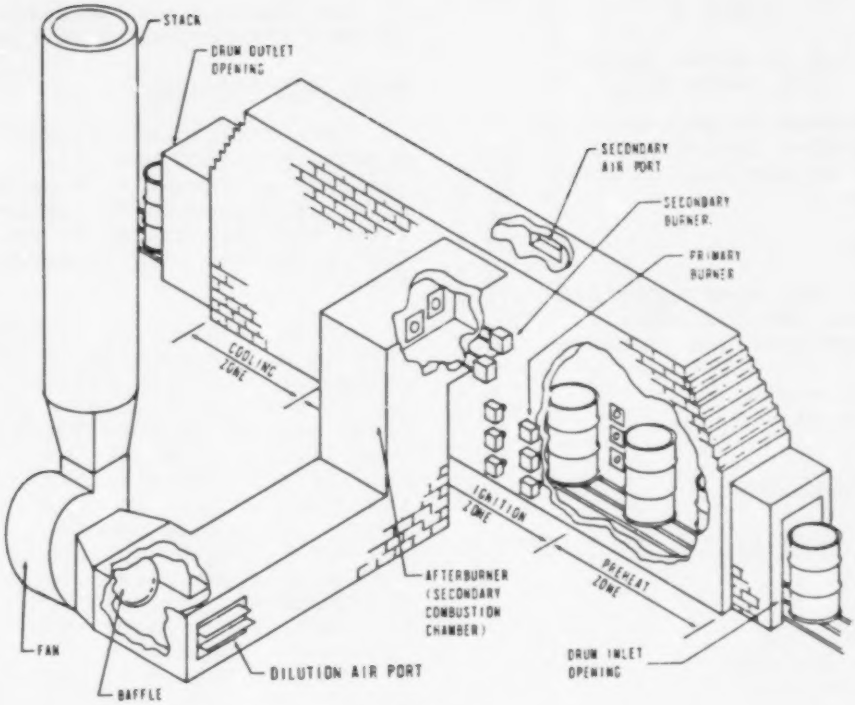

STACK
DRUM OUTLET OPENING
SECONDARY AIR PORT
SECONDARY BURNER.
PRIMARY BURNER
COOLING ZONE
IGNITION ZONE
PREHEAT ZONE
AFTERBURNER (SECONDARY COMBUSTION CHAMBER)
FAN
BAFFLE
DILUTION AIR PORT
DRUM INLET OPENING

FIGURE 3

TYPICAL DRUM RECLAMATION FURNACE WITH AFTERBURNER

(Reference No. 4)

water quenched. About 40 percent of burning plants have the capability to quench, but not all use it all the time. Some only operate the water quencher when smoky drums are being burned, or when there is a visible emission from the drum outlet opening. After cooling, open head drums are shot blasted, dedented, leak tested, lined, and painted.

Natural gas is the preferred furnace fuel. Where it is unavailable or uneconomical, No. 2 oil is recommended.

Operating Procedures

Most reconditioners have established procedures for drum receiving and storage, and nearly two-thirds have oil recovery systems. At a typical plant, about 22,700 liters (6,000 gallons) of oil are recovered monthly.

About 5.4 percent of drums bound for reconditioning eventually are discarded. The bulk of these are sold for scrap.

Almost all reconditioners refuse to accept drums containing certain materials (Table 3). Pesticides are refused by 83 percent of reconditioners. Other drums frequently refused are those formerly containing ink and adhesives. The industry processes over 200,000 used pesticide drums per year, although there is some uncertainty in this figure. Most are burned, but a few plants do wash significant numbers of pesticide drums. Even though the industry claims that few facilities accept pesticide drums, most plants have such drums scattered within their inventories.

Plants that process pesticide drums on a regular basis use special handling and processing procedures.

TABLE 3

TYPES OF DRUMS REUSED
FOR PROCESSING

(expressed as percentage of
companies having restrictions)

Pesticides	83.0
Ink	29.8
Adhesives	27.7
Paint	14.9
Toxic and Hazardous Materials	12.8
Mercaptans, TDI and other Unneutralized Gas Odorants	10.6
Resins	8.5
Class B Poisons	6.4
Odorous Materials	6.4
Tar/Asphalt	4.3
PCB	4.3
Cadmium Compounds	4.3

The following are 2% or less:

- Delaware Drums
- Heavy Drums
- Plastic Inserts
- Excessive Residual
- Unknown Contents
- Smokers
- Automobile Sound Deadener
- Silicone
- Acrylics
- Carbon Disulfide
- Chlorides
- Cyanides
- Mercury Compounds
- Sodium
- Sulfur Monochloride
- Zinc Compounds
- Formaldehyde
- Organic Phosphates
- Benzidine and its Salts
- Dye
- Industrial Chemicals
- Carcinogens
- Radioactive Materials

Results reported by others indicate that burning (using afterburners at 900°C or 1650°F) effectively detoxifies most pesticide drums (5). Additionally, in washing plants, phosphorus and nitrogen-containing pesticides lend themselves to detoxification by alkaline hydrolysis. Many unanswered questions are expected to be dealt with as results of the sampling and analysis portion of this EPA project become available.

Pollutant Loadings

The EPA project placed most emphasis on liquid and solid wastes in terms of pollutant sources and pathways. Previous investigations indicated that air emissions presented little problem in drum reconditioning.

Most washing facilities either recycle and reuse caustic and rinse waters or discharge effluents into public sewerage systems. Table 4 shows various methods for dealing with liquid waste streams. About half of all plants (including those that burn), claim to discharge some water into public sewers. Nearly 20 percent of washing plants claim to have completely closed cycle or "zero discharge" systems. Only 10 percent are direct dischargers after treatment. Mean flow for a typical facility is 56,800 liters (15,000 gallons) per day. Because such a high percentage of plants discharge to sewers, water quality limitations for such discharges become very important. Typical limitations as determined during the recent NABADA survey are shown in Table 5.

Reconditioning wastewater is characterized by high pH, COD, BOD, and solids values. These and other wastewater data are given in Table 6. There is wide variability in wastewaters depending upon the types of drums processed. Some of the mean values shown in Table 6 are skewed by one or more outlying data points. Hence, the data set for each of the parameters in Table 6 was examined to determine which values were outside of the 99 percent confidence level. Eleven of the 58 showed that some values were outside of this confidence limit. Such values were discarded and a new analysis made. The process was repeated until all data sets conformed to the 99 percent confidence limit. The statistically adjusted discharge values are given in Table 7. This is not to imply that these values are better or worse than those in Table 6.

TABLE 4

METHODS FOR DEALING WITH LIQUID WASTE STREAMS

METHOD	PERCENTAGE OF RECONDITIONERS USING THE METHOD		
	Caustic Solution	Rinse Water	Runoff
Discharge to public sewer	7.8	42.5	42.9
Neutralize and discharge to public sewer	13.7	-	-
Discharge to stream	0	2.5	21.4
Recycle and reuse	52.9	35.0	-
Treat at own treatment plant and discharge to stream	2.0	10.0	35.7
Discharge some and recycle some	21.6	-	-
Haul to landfill	2.0	7.5	-
Evaporate	-	2.5	-
TOTAL	100.0	100.0	100.0

TABLE 5

WATER QUALITY LIMITATIONS
FOR DISCHARGES TO PUBLICLY
OWNED SEWERAGE SYSTEMS

Parameter	No. of Reported Limitations	Mean Value*	Range* Low	Range* High
BOD (biochemical oxygen demand)	12	229	20	no limit
COD (chemical oxygen demand)	5	345	25	450
Suspended Solids	12	266	25	no limit
Total Dissolved Solids	4	625	500	1000
pH	13	5.3 to 9.8	4.5	10.5
Oil and Grease	11	162	0	1000
Fats and Oils	2	100	100	100
Fuel Oil	1	0	-	-
Benzene	1	0	-	-
Cyanides	8	2.1	0.1	10
Formaldehyde	1	5.0	-	-
Gasoline	1	0	-	-
Naphtha	1	0	-	-
Pesticides	4	0	-	-
Phenol	5	0.5	0.3	0.5
Volatile Organics	1	5.0	-	-
Chlorides	1	250	-	-
Fluorides	1	0	-	-
Phosphates	2	21	12	30
Total Kjeldahl Nitrogen	1	no limit	-	-
Temperature	6	140°F	110°F	150°F
Antimony	5	1.0	0	5.0
Arsenic	7	0.2	0.05	0.5

TABLE 5 (con't)

Parameter	No. of Reported Limitations	Mean Value*	Range* Low	High
Barium	7	2.9	1.0	5.0
Beryllium	4	0.3	0	1.0
Bismuth	4	0.3	0	1.0
Boron	4	0.6	0.5	1.0
Cadmium	10	1.1	0.002	3.0
Chromium (total)	9	6.5	0.05	25
Chromium (hexavalent)	6	0.7	0.05	1.0
Cobalt	4	0.05	0	0.2
Copper	9	1.0	0.2	3
Iron	6	4.0	1.0	5.0
Lead	11	0.9	0.1	5
Manganese	7	2.0	0.05	5.0
Mercury	5	0.007	0	0.02
Molybdenum	4	0.03	0	0.1
Nickel	9	2.4	0.5	10
Rhenium	4	0.1	0	0.5
Selenium	7	0.6	0.02	2.0
Silver	7	1.1	0.05	5.0
Strontium	4	0.1	0	0.5
Tellurium	4	0.1	0	0.5
Tin	4	0.8	0	1.0
Uranium	1	0	-	-
Zinc	11	5.4	1.0	15

* Values reported in milligrams/liter unless specified otherwise.

TABLE 6

WASTEWATER DISCHARGE ANALYSES*

PARAMETER	No. of Observations	Mean	Standard Deviation	Range	
				Low	High
Aluminum	2	181.5	195.9	43	320
Antimony	6	0.3	0.4	0	1
Arsenic	3	0.13	0.23	<0.03	0.40
Barium	3	9.3	9.0	<1.0	10
Beryllium	3	0	0	0	0
Bismuth	2	0	0	0	0
BOD_5	31	4,599	9,882	10	44,133
Boron	4	2.5	4.3	<0.05	8.9
Bromide	1	0	-	-	-
Cadmium	12	0.10	0.26	0.0002	0.90
Calcium	4	74	60	28	162
TOC	5	5,397	8,455	71	20,412
COD	24	24,549	64,889	91.5	310,909
Chloride	6	2,169	1,540	6.7	4,144
Chromium (total)	26	12.5	43.3	0.023	224
Chromium (hexavalent)	4	0.11	0.12	0	0.22
Cobalt	2	0.2	0.2	0	0.3
Color (Pt/Co units)	3	420	312	60	600
Copper	16	2.4	5.7	0	23.0
Cyanide (total)	7	1.4	2.0	0.2	5.9
Cyanide ("A")	5	0.5	0.4	0.2	1.2
Fluoride	1	1.2	-	-	-
Iron	12	114	294	1.6	1,041
Lead	29	45.8	154.5	0	682
Magnesium	4	23	21	5.5	54
Manganese	4	1.5	2.4	0	5
Mercury	11	1.0	1.9	0	5.9
Molybdenum	3	0	0	0	0
Nickel	12	0.3	0.4	0	1.0
Nitrogen (Total Kjeldahl)	4	18.6	15.3	6.2	40

"continued"

TABLE 6 (con't)

PARAMETER	No. of Observations	Mean	Standard Deviation	Range	
				Low	High
Nitrogen (Ammonia)	4	13.3	10.8	1.96	23
Nitrogen (Nitrate)	5	4.6	5.1	0.66	13.2
Oil and Grease	37	10,228	42,656	19.2	248,340
pH	39	10.9	3.3	1.8	13.6
Phenols	21	43.8	45.5	0.044	148
Phosphorus (total)	8	34.3	25.1	5.04	68.48
Potassium	2	33	15	22.0	43
Selenium	4	0.12	0.23	0	0.47
Silicon	3	75	33	37	94
Silver	4	0.01	0.02	0	0.04
Sodium	4	10,157	9,643	1,678	19,000
Strontium	2	0	0	0	-
Sulfate	4	7,747	8,384	16	15,000
Sulfide	3	14.6	22.1	0.7	40.0
Sulfite	1	<1	-	-	-
Surfactants(MBAS)	2	2.0	1.6	0.8	3.1
TDS	4	8,514	9,264	944	22,000
Total Solids	7	8,701	12,013	970	35,000
Total Fixed Solids	1	5,414	-	-	-
Total Suspended Solids	46	2,435	4,113	77	24,000
Total Volatile Solids	2	265	92	200	330
Mineral Suspended Solids	1	32	-	-	-
Volatile Suspended Solids	1	108	-	-	-
Thallium	1	<0.1	-	-	-
Tin	6	1.1	2.4	0	6
Titanium	2	115	163	0	230
Turbidity(NTU)	3	33	10	21	39
Zinc	33	24.0	46.5	0.1	228

* All values in milligrams/liter unless specified otherwise.

TABLE 7

STATISTICALLY ADJUSTED DISCHARGE VALUES*

Parameter	No. of Observations	Mean	Standard Deviation	Range Low	Range High
BOD_5	27	1,262	899	10	3,617
Cadmium	11	0.03	0.06	0	0.15
COD	19	4,011	2,835	91.5	8,638
Chromium (total)	25	4.0	4.0	0.023	11.0
Copper	14	0.7	0.8	0	2.5
Iron	11	29.3	34.0	1.6	54
Lead	24	2.1	2.2	0	6.7
Oil and Grease	33	901	1,202	19.2	3,970
pH	37	11.4	2.7	4.8	13.6
Total Suspended Solids	44	1,669	1,662	77	5,195
Zinc	30	10.5	8.6	0.1	34

* All values in milligrams/liter unless specified otherwise

It merely means that outlying values have been discarded in an attempt to present values which potentially could be more typical.

There is some evidence of hazardous organics in small concentrations in some reconditioning wastewater.

The biggest problem facing reconditioners is the need to provide safe, economical, and environmentally acceptable means for residuals management. Evolving solid and hazardous waste management regulations are expected to have major impact on the industry. Disposition methods for drum residue are shown in Tables 8 and 9. Clearly, landfilling has been and continues to be the predominant method for residue disposal. Use of incineration is increasing and will continue to at an accelerated rate as the impact of RCRA regulations are felt.

On the average, drums received by reconditioners contain 2.5 liters (0.65 gallons) or 2.5 kilograms (5.4 pounds) of residues. As Table 10 reveals, caustic sludges have high pH, COD, BOD, and oil and grease concentrations, much as caustic washing solutions, but in far greater amounts.

Presently, surface runoff at reconditioning facilities is not being handled to any extent.

TABLE 8

RESIDUE DISPOSAL METHODS BY REGION IN 1973

METHOD	PERCENTAGE OF RECONDITIONERS USING THE METHOD			
	Eastern Region	Central Region	Western Region	Total U.S.
Landfill	58.3	72.5	80.0	67.3
Burn and landfill				
- on-site	8.3	-	-	3.4
- off-site	16.7	13.8	20.0	15.6
- no residue	8.3	6.9	-	6.9
Discharge to sewer	4.2	-	-	1.7
Store	4.2	-	-	1.7
Contract burning	-	3.4	-	1.7
Contractor hauling	-	3.4	-	1.7
TOTAL	100.0	100.0	100.0	100.0

TABLE 9

METHODS FOR DEALING WITH RESIDUES (NABADA SURVEY)

METHOD	PERCENTAGE OF RECONDITIONERS USING THE METHOD		
	Concentrated Liquid Drainage	Sludges and Solid Drainage	Burned Ash
Discharge to sewer	6.0	1.9	-
Contractor hauling	40.0	38.5	32.3
On-site land disposal	4.0	7.7	-
On-site burning	16.0	-	-
Landfill off-site	24.0	36.5	38.7
Return to emptier	2.0	1.9	3.2
Burn and landfill	-	5.8	-
Dispose with other sludges	-	-	25.8
Store	-	1.9	-
Own treatment plant	6.0	-	-
Drain to caustic solution	2.0	-	-
Off-site burning	-	5.8	-
TOTAL	100.0	100.0	100.0

TABLE 10

CAUSTIC SLUDGE COMPOSITION*

Parameter	No. of Observations	Average	Range Low	Range High
pH	6	12.3	11.4	13.2
Oil and Grease	5	117,654	3,826	240,000
Floating Oil	1	323.7	-	-
TDS	3	192,533	110,000	314,600
Total Solids	5	368,047	11,837	547,000
Suspended Solids	4	150,822	2,150	394,000
BOD	1	12,000	-	-
COD	1	580,000	-	-
TOC	3	174,333	35,000	420,000
Arsenic	2	1.64	0	3.28
Barium	1	651	-	-
Cadmium	4	9.6	1.9	13.5
Calcium	1	1,687	-	-
Chlorides	2	1,390	880	1,900
Chromium (total)	6	199	0.01	469
Chromium (hexavalent)	2	0.64	0.009	1.28
Copper	4	2,393	22	9,000
Cyanides	4	10	3.0	19
Fluorides	2	17.5	9.0	26
Iron	4	24,922	1,087	76,800
Lead	4	4,554	375	15,100
Manganese	2	290	30	550
Mercury	4	0.48	0.00147	1.51
Nickel	5	29.2	0.83	82
Phenol	4	199	19.05	500

TABLE 10 (con't)

Parameter	No. of Observations	Average	Range	
			Low	High
Phosphates	2	7,500	2,100	12,900
Potassium	1	2,010	-	-
Selenium	2	30.5	8.7	52.3
Silica	2	5,325	3,300	7,350
Silver	4	2.3	0.5	5.6
Sodium	1	8,455	-	-
Sulfates	1	12,300	-	-
Zinc	6	6,791	25.95	39,000
Specific Weight	1	10.08	-	-
Flash Point	1	>210°F	-	-
Ash Content	1	14.36%	-	-

*All values in milligrams/liter unless specified otherwise.

Pollution Control Practice and Costs

Major potential alternatives for air pollution control at drum reclamation furnaces are: 1) direct combustion in the 650°C (1200°F) to 900°C (1650°F) temperature range with an afterburner residence time of 0.3 to 0.7 seconds; 2) catalytic oxidation in the 315°C (600°F) to 510°C (950°F) range; 3) sorption using activated carbon, silica gel or other materials; and 4) scrubber systems. Worldwide, the direct combustion and afterburner method is the one most frequently used. Other methods usually are adjuncts to this primary method.

All U.S. reconditioning drum furnaces have afterburners to consume particulates and organics not burned in the furnace main chamber. About 37 percent of drum burning facilities use air pollution control equipment and techniques in addition to afterburners. Typically, equipment includes scrubbers, packed towers, baghouses, and dust collectors. Some methods used to optimize existing equipment are automatic ducts to regulate air flow, and entry and exit air curtains for better and more efficient combustion.

For washing plants, about 55 percent have in-place or under construction their own wastewater treatment plants. Table 11 lists equipment used by reconditioners, some of which is related to water pollution control. Other equipment mentioned in the NABADA survey was coalescing plate separators for oil removal, oil skimmers (often the endless belt or rope type), and packaged wastewater treatment systems. Only two manufacturers have sold a significant number of pollution control devices to the industry: one is a diatomaceous earth filter, and the other is a dissolved air flotation rinse water clarification system.

Many reconditioners fabricate their own pollution control systems as opposed to using commercially available products. Operating procedures such as preflushing, stream segregation, and cascading water use are important adjuncts to pollution control equipment.

TABLE 11

WASHING PLANT RECONDITIONING EQUIPMENT

Equipment Type	Percentage of Reconditioners Using Such Equipment
Flushomatics$^{(TM)}$	26.8
Caustic Filters	31.7
Vacuum Drying Systems	73.2
Automated Flushers	48.8
Automated Upenders	80.5
Oil/Water Separators	61.0
Screens for Gross Particle Removal	56.1
Dissolved Air Flotation	17.1
Flocculation/Sedimentation	34.1
Coagulation Feeders	7.3

Table 12 lists new drum prices for the year 1977 and 1978, as well as prices for March of 1979 and 1980. Figures were taken directly from the M34K reports of the Bureau of the Census. Prices of new and reconditioned drums also were part of the NABADA survey. These data are reported in Table 13. Note that the NABADA survey prices do not reflect drum gage or condition. Figures, however, compare well with those in Table 12.

A typical reconditioner pays about $400 per month in sewer surcharges. The bases for surcharges at several locations are shown in Table 14.

Almost 90 percent of water used by reconditioners is purchased from local public or private water distribution systems at an average [illegible] of $0.23/1000 liters ($0.86/gallons). Other utility costs, principally gas and electricity, average approximately $66,000 per year for a typical plant.

Average residue disposal costs are $0.15 to $0.17 per reconditioned drum.

Based upon the recent NABADA survey, it is estimated that U.S. reconditioners have about $12,700,000 of installed pollution control equipment. Of this amount about $9,100,000 is undepreciated (based upon 10-year life and straight-line depreciation). Hence, it is clear that most of the equipment is fairly new. Table 15 identifies types of pollution control equipment along with estimated capital costs and depreciation.

The NABADA survey determined that a typical reconditioning facility spends about $45,000 annually for operations and maintenance related to pollution control. Table 16 shows the distribution of these expenditures. Most of the costs for afterburners are for supplemental fuel.

A question on the NABADA survey asked for approximate unit costs per drum for pollution control. Responders claimed costs of $0.38/drum for washing and $0.35/drum for burning. An attempt was made to verify this figure in the following way. Component costs are: capital amortization, operations and maintenance costs, and residual disposal costs.

TABLE 12

PRICES OF NEW DRUMS
(Bureau of the Census Survey)

	PRICE (in dollars)*			
	March 1980	March 1979	Year 1978	Year 1977
Tight Head				
18 gage and heavier	18.07	17.26	16.51	15.50
19 and 20 gage**	18.39	16.86	16.33	14.43
Open Head				
18 gage and heavier	22.37	19.33	18.42	17.77
19 and 20 gage**	16.82	15.60	14.71	13.97

* Drum price is at the point of production. It includes the net sales price, f.o.b. plant, after discounts and allowances, exclusive of freight charges and excise taxes.

** Includes 20/18 gage drums.

TABLE 13

PRICES OF NEW AND RECONDITIONED DRUMS
(NABADA Survey)

Drum Type	Mean Price ($)	Standard Deviation	Range	
			Min.	Max.
New Tight Head	17.47	2.66	13.50	27.00
New Open Head	19.42	4.31	15.00	34.00
Reconditioned Tight Head	11.74	1.33	9.00	15.19
Reconditioned Open Head	11.89	1.79	9.75	15.50
Laundry/Service Fee	5.78	1.18	4.00	9.80

TABLE 14

BASES FOR SEWERAGE SURCHARGES

Volume Cost Factor (¢/1000 gal)	BOD Cost Factor (¢/pound)		TSS Cost Factor (¢/pound)		TKN Cost Factor (¢/pound)		COD Cost Factor (¢/pound)	Other Costs
		less exclusion (mg/l)		less exclusion (mg/l)		less exclusion (mg/l		
26.7	-		2.0	0	-		2.0	-
-	4.3	305	3.3	400	-		-	-
11	3.0	0	7.9	0	-		-	Sewer Connection Charge = $4.53/mo.
92	5.6	300	5.6	300	-		-	Minimum Bill= $25.00/mo.
69.3	7.9	250	8.6	250	-		-	-
-	4.6	240	3.1	300	5.5	25	-	If a pollutant is less than 80% of the exclusion value, then there may be a credit against the total surcharge.
25.4	-		-		-		-	Flat infiltration - inflow charge=25.4¢/ 1000 gal/mo.
Ave 44.9	5.1	219	5.1	208				

TABLE 15

POLLUTION CONTROL EQUIPMENT
(in thousands of dollars)

Equipment Type	Capital Cost	Undepreciated Cost
Incinerators/Afterburners	5,100	3,600
Dust Collectors/Scrubbers	400	220
Paint and Spray Controls	970	580
Water Pretreatment & Treatment	4,740	3,620
Tanks & Clarifiers	830	580
Dissolved Air Flotation	430	340
Auxiliary Water Pollution Equipment	61	44
Water Filtration	170	138
Evaporator	34	17
TOTAL	12,735	9,139

TABLE 16

OPERATIONS AND MAINTENANCE COSTS FOR POLLUTION CONTROL
(in thousands of dollars)

O & M Category	Annual O & M Cost
Incinerators/Afterburners	1,880
Dust Collectors/Scrubbers	28
Paint and Spray Controls	148
Water Pretreatment & Treatment	2,840
Tanks & Clarifiers	306
Dissolved Air Flotation	142
Auxiliary Water Pollution Equipment	3
Other	107
TOTAL	5,454

Installed capital of $12,735,000 (from Table 15) at 8 percent interest (from 1977) for 10-year useful life was used to allocate amortization allowance. For 41,204,000 drums, the per drum cost is $0.067. Operations and maintenance costs from Table 16 yield a per drum cost of $0.132. Residue disposal costs for landfilling cited earlier were about $0.16. The total of these three elements is $0.36/drum.

Values cited by reconditioners at technical forums have been updated to current costs. These are $0.37/drum for U.S. reconditioners and $0.44/drum for Japanese. Hence, it appears that NABADA survey figures are accurate. Additionally, it implies that reconditioners have good insight into various cost components.

References

1. U.S. Census of Wholesale Trade: 1972. Commodity Line Sales, Report WC 72-L, U.S. Department of Commerce. November 1975.
2. Current Industrial Reports. Steel Shipping Drums and Pails, Bureau of the Census, M34K(79)-12 Report. U.S. Department of Commerce. February 1980.
3. Checchi Report for the National Barrel and Drum Association,Inc. Checchi and Associates, Washington, D.C. 1973.
4. Danielson, John A., Editor. Air Pollution Engineering Manual (Second Edition), Air Pollution Control District, County of Los Angeles, Report AP-40, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1973.
5. Wilkinson, R.R., G.L. Kelso, and F.C. Hopkins. State-of-the-Art Report: Pesticide Disposal Research. EPA-600/2-78-183, U.S. Environmental Protection Agency, Cincinnati, Ohio, September 1978.

BENCH SCALE ASSESSMENT OF CONCENTRATION TECHNOLOGIES FOR HAZARDOUS AQUEOUS WASTE TREATMENT

Alan J. Shuckrow
Andrew P. Pajak
Touhill, Shuckrow and Associates, Inc.
Pittsburgh, Pennsylvania 15237

ABSTRACT

This paper describes portions of the experimental phase of an ongoing program to evaluate the applicability of several concentration technologies to treatment of hazardous aqueous wastes. Studies are being carried out at the Ott/Story site in Muskegon, Michigan using groundwater which has been severely contaminated by numerous organic compounds. Specifically, bench scale laboratory treatability studies including activated carbon adsorption, resin adsorption, aerobic and anaerobic biological treatment, and stripping are under investigation. Most treatment technologies studied to date have been moderately effective in reducing the levels of organic contamination. However, a process train consisting of granular activated carbon adsorption followed by activated sludge treatment can achieve high levels of treatment for short periods of time. Virtually complete removal of organic priority pollutants can be achieved under some conditions.

Introduction

The objective of the project discussed in this paper is to identify and evaluate technologies for concentrating hazardous constituents of aqueous waste streams. As reported previously (2,3), this objective is being met through a multi-phased program involving literature review, desktop evaulations, and laboratory bench scale treatability studies.

Early in this project it was concluded that the major hazardous waste problem facing the public sector is contamination from waste disposal sites, specifically leachates and contaminated ground and surface waters. Wastewater compositions, however, are diverse and often vary at a given site. Moreover, few actual applications of treatment technology to this type of hazardous aqueous waste problem exist.

On the basis of an extensive literature review and desktop analysis of concentration technologies, the following unit processes were identified as having potential broad application to the aqueous contamination problems associated with waste disposal sites:

- Biological treatment
- Chemical coagulation
- Carbon adsorption
- Membrane processes
- Resin adsorption
- Stripping

These, however, must be supplemented with ancillary processes such as sedimentation and filtration.

Since hazardous aqueous waste streams vary widely in composition and often contain a diversity of constituents, in general, no single unit process is capable of providing optimum treatment. Rather, arrangement of individual processes into process trains is necessary to achieve high levels of treatment in the most cost-effective manner. Thus, having identified the most promising unit concentration technologies, the next step was to formulate process trains which combined technologies in a fashion which would provide broad spectrum treatment capability. The objective was to identify process trains which would produce high quality effluents when applied to the wide range of waste stream compositions likely to be encountered. Five such process trains incorporating the selected concentration technologies were formulated. Details describing the selection of these unit processes and the five process trains previously have been reported (2).

Subsequent to the desktop technology evaluations, experimental treatability studies were initiated. These experimental investigations are described below.

Bench Scale Studies

Several alternative approaches for conducting laboratory evaluations of the unit process identified earlier were considered. Actual, rather than synthetic, wastewater was the desired feedstock because the complexity of wastewater composition at the various hazardous waste problem sites could not be duplicated adequately by a synthetic wastewater.

On the basis of several factors, including availability of quantitative data describing problem nature and magnitude, absence of pending litigation which would limit information transfer, cooperative relationships between current site owners and the regulatory agencies, and an ongoing feasibility study to identify and evaluate clean-up techniques being conducted by the state agency, the Ott/Story Chemical Company site (now owned by Cordova Chemical Company) in North Muskegon, Michigan was selected. Groundwater in the area had been contaminated by the disposal and poorly controlled storage of chemical production wastewaters by previous facility owners. Because of possible changes in wastewater composition during shipment and prolonged storage, and logistics problems associated with shipment of the substantial quantities of wastewater required, a treatability laboratory was established at the site.

The characteristics of groundwater at the Ott/Story site are shown in Table 1. In addition to these major pollutants, more than 70 other organic pollutants were detected at concentrations > 10 μg/l. Organic compounds are the primary pollutants; heavy metal concentrations are believed not to be a problem.

TABLE 1. GROUNDWATER QUALITY AT OTT/STORY SITE

Conventional pollutants:	
pH	8 - 12
COD	5400 mg/l
TOC	400 - 1500 mg/l
NH_3-N	64 mg/l
Major priority pollutants:	
Vinyl chloride	*ND - 32,500 μg/l
Methylene chloride	< 5 - 6,570 μg/l
1,1-Dichloroethylene	60 - 19,850 μg/l
1,1-Dichloroethane	< 5 - 14,280 μg/l
1,2-Dichloroethane	350 - 111,000 μg/l
Benzene	ND - 7,370 μg/l
1,1,2,2-Tetrachloroethane	< 5 - 1,590 μg/l
Toluene	< 5 - 5,850 μg/l

* Not Detectable

In designing the bench scale studies, it was decided to first examine unit processes and subsequently, as a data base was developed, to evaluate process trains. The bench scale evaluation approach is outlined below:

1. Pretreatment investigations
   a. neutralization
   b. chemical coagulation and precipitation
   c. solids/liquid separation
   d. air sparging
2. Batch studies
   a. carbon adsorption
   b. resin adsorption
3. Batch sequential studies
   a. air sparging followed by carbon adsorption
   b. carbon adsorption followed by

    air sparging
  c. carbon adsorption followed by resin adsorption
4. Continuous flow studies
  a. steam stripping, packed bed column
  b. granular activated carbon columns
  c. biological treatment
  d. biophysical treatment

Results from pretreatment investigations, batch studies, and batch sequential studies have been reported previously (1). To briefly summarize:

- Results on major priority pollutant removals measured in these studies are summarized in Table 2.

- Carbon adsorption reduced almost all organic priority pollutants to less than GC/MS detection limits.

- Resin sorption proved to be only slightly less effective than carbon sorption. Most organic priority pollutants were reduced to below detection limits; all were reduced by at least 98%.

- All volatile organic priority pollutants were reduced to less than detection levels by air stripping. Removals for other organic priority pollutants ranged from 4 to 96%.

- Carbon treatment of the air sparged groundwater generally resulted in reduction to less than detection limits for the remaining organic priority pollutants. All were reduced by more than 98%.

- Despite good removals of priority pollutants, a significant residual TOC (301-455 mg/l) was measured in all treated samples. This residual represents unidentified non-priority organic pollutants.

The remainder of this paper describes continuous flow studies which have been conducted or are in progress. Because study efforts will continue until mid-1981, the results are incomplete and should be considered as preliminary subject to further investigations.

Steam Stripping

Continuous flow, steam stripping experiments were conducted using a 76.2 cm by 4.8 cm (ID) packed column. The apparatus was operated at feed stream flow rates of 40 to 80 ml/min, overhead (condensate) flow rates of 3.5 to 9.2 ml/min (overhead to feed flow ratios of 0.064 to 0.14), no reflux flow, feed stream TOC concentrations of 480 to 610 mg/l, and durations of 1 to 4 hours after establishing steady state operation within the available operational controls.

As indicated in Figure 1, which illustrates the results of these studies, TOC concentration in the bottoms ranged from 300 to 400 mg/l and appeared to be independent of the overhead:feed ratio. Average TOC reduction between feed and bottoms was 34%. These observations indicate a major constraint associated with steam stripping - it is necessary to further treat a bottoms waste stream having a flow only slightly less than the feed flow. It should be noted that maintaining steady state operation of the apparatus proved to be very difficult. The minimum overhead to feed flow ratio which could be achieved was 0.064, significantly higher than the desirable range of 0.02 to 0.05. It was concluded that, because bottoms TOC concentration appeared to be independent of system flow rates and feed TOC levels over the ranges examined and because additional treatment of the bottoms is necessary, steam stripping would likely be a costly, yet only moderately effective, concentration process.

Adsorption - Granular Activated Carbon and Resin

Continuous flow granular activated carbon (GAC) studies were conducted at the unadjusted groundwater pH (9.3 to 10.0) using Filtrasorb

TABLE 2. TOC AND MAJOR ORGANIC POLLUTANT REMOVALS DURING BATCH SEQUENTIAL STUDIES

	Study 1 (mg/l)			Study 2 (mg/l)		
Compound	Raw Waste	Resin Sorption Effluent	Carbon Sorption Effluent	Raw Waste	Air Sparge Effluent	Sparge plus Carbon Sorption Effluent
TOC	638	455	332	720	641	301
Benzene*	7.8	0.17	0.01	5.3	ND	ND
Benzoic Acid	0.17	ND	0.18	0.30	0.02	ND
Camphor	4.0	0.04	ND	3.9	0.47	0.01
Chloroform*	1.4	ND	ND	2.0	ND	ND
1,1-Dichloroethane*	1.2	ND	ND	1.6	ND	ND
1,2-Dichloroethane*	111	0.23	0.01	14	ND	0.01
1,1-Dichloroethylene*	0.06	ND	ND	1.0	ND	ND
Dimethylaniline	17.0	0.25	ND	15.0	0.61	0.08
Ethylaniline	3.3	ND	ND	3.8	0.60	ND
Methylene Chloride*	0.06	ND	ND	0.07	ND	NA
Toluene*	2.6	ND	ND	3.6	ND	ND

(Note: 27 organic pollutants detected at 0.01 to 0.31 mg/l; none found in effluents.)

ND - Not Detected at detection limit of 0.010 mg/l

NA - Not Analyzed

* - Priority Pollutant

300 GAC. The studies used three or four glass columns arranged in series with sampling ports located at the influent and effluent ends of each column. Each column is 122 cm by 2.54 cm (ID) with 91.4 cm of GAC in each column. The system was operated in a downflow mode at a loading rate of approximately 1.35 l/m^2s (2 gpm/ft^2). This provided an empty bed contact time (EBCT) of approximately 15 minutes per column. Influent TOC concentration varied substantially, ranging from 316 to 950 mg/l.

Results of a typical study are illustrated in Figure 2. Results are reported as removal percentage rather than effluent concentration because of influent TOC fluctuations. Generally, after only 3 to 10 bed volumes (BVs), TOC removal decreased to 50%. TOC leakage reached 90% after about 200 to 240 BVs were processed and continued at this level until up to 500 BV had been processed. As would be expected, effluents from columns 2 and 3 are intermediate between columns 1 and 4. Available GAC column performance data corresponds to batch sorption study data.

Continuous flow resin

investigate a combined sorption/biological system. The rationale employed was to attempt to utilize the sorbent to protect the biological system from toxic materials. Thus, the sorbent could be allowed to leak relatively high concentrations of organics which would be degraded in the subsequent biological process. Two such process trains were investigated:

1. FS 300 granular activated carbon followed by activated sludge (GAC/AS), and

2. XE-347 resin followed by activated sludge (RES/AS).

Operating conditions for the GAC/AS process trains are summarized below:

- GAC - three 91.4 cm by 2.54 cm columns in series, 0.0815 $m^3/m^2/d$ (2 gpm/ft^2) hydraulic loading, and 34 min EBCT

- AS - one liter reactors with hydraulic retention times (HRT) of 6 to 16 hr; GAC effluent neutralized and nutrients added; mixed liquor suspended solids ranged from about 2000 to 8000 mg/l; and 5000 mg/l PAC in aeration chamber during PAC studies.

Performance of this process train under various conditions is illustrated in Figure 3. It should be noted that the GAC process was operated approximately 6 hr/day, five days per week whereas the AS process was operated continuously. This necessitated collection and storage of GAC effluent for 1 to 3 days to maintain continuous feed to the AS reactors. Some decrease in TOC levels were noted during the storage periods. Losses most likely were due to volatilization and/or biological degradation. Thus, it is assumed that similar reductions would have occurred in the AS reactors. The following observations have been made on the basis of data presented in Figure 3:

- GAC pretreatment of raw groundwater permits development of a culture of aerobic organisms capable of further treating GAC effluent. In excess of 95% TOC removal can be achieved by this process during the period which GAC removal of TOC exceeds 30%. After this initial period, process train performance declines as GAC performance declines. Effluent TOC could be maintained at < 100 mg/l only for short time periods and only when GAC performance was at its peak.

- These data indicate that some fraction of TOC which initially is sorbed by GAC begins to leak through the system after a short period of operation. This fraction of TOC which leaks through the GAC system is not toxic to AS but does not appear to be removed or reduced either biologically or by air stripping associated with AS aeration.

- Operation of the AS process at HRTs ranging from 6 to 16 hr, with or without powdered activated carbon added to the aeration chamber seems to have little impact on process performance (based upon TOC removal).

- Overall system performance was maintained at 75-85% TOC removal (effluent TOC of 100 to 185 mg/l) for about 21 days (46 retention times for AS and > 110 BVs for GAC).

- Visual observations and typical mixed liquor analyses (MLSS and MLVSS) suggest that the biological systems could survive in and utilize GAC pretreated groundwater even after GAC performance had declined to about 10% TOC removal. However, AS effluent contained about

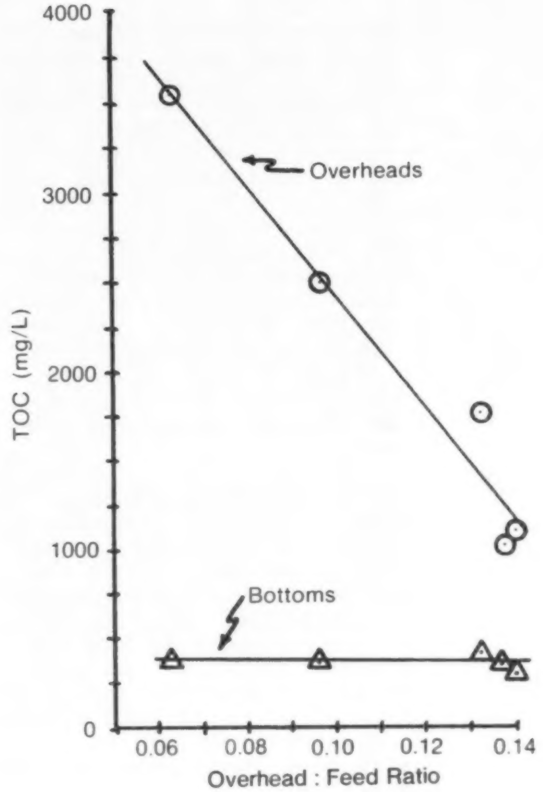


Figure 1. Results of steam stripping studies.

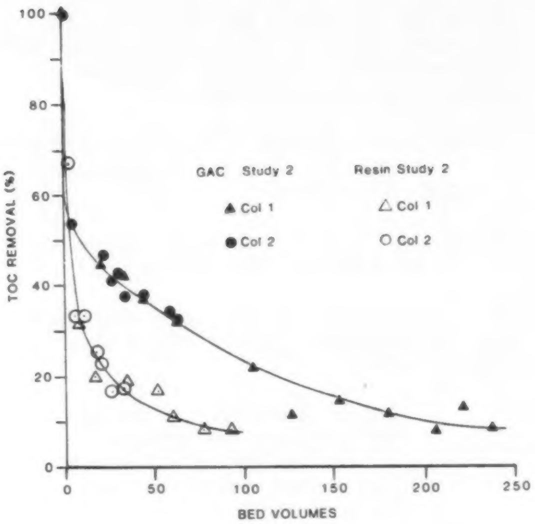


Figure 2. TOC removal by adsorption.

adsorption studies were conducted using XE-347 carbonaceous resin. Three columns similar to those used for GAC studies were charged with 792 to 835 cm^3 of resin and were operated at loading rates of 2.95 to 3.79 BV/hr. EBCT ranged from 16 to 20 min. TOC breakthrough data for one representative study are shown in Figure 2. Breakthrough characteristics were similar to those of GAC except that XE-347 TOC removal declined more rapidly. TOC removal diminished to < 50% after about 5 BV were processed and appeared to stabilize at about 10% for at least 120 BV.

Biological Treatment

Several attempts were made to acclimate an activated sludge culture to raw groundwater using 350 ml reactors. All attempts, however, were minimally successful. Neither a conventional activated sludge nor a commercial microbial culture could be acclimated. Slight loading fluctuations encouraged growth of a light colored, filamentous biomass which settled poorly. About 60% TOC reduction was achieved; however, stripping due to aeration appeared to account for about two-thirds of this removal. Addition of trace elements and nutrients, and pH adjustment to pH 7.0 to 7.5 did not aid acclimation to raw groundwater. Addition of powdered activated carbon (PAC) at aeration chamber concentrations of about 10,000 mg/l also did not aid acclimation to raw groundwater or improve TOC removal or mixed liquor appearance.

Adsorption/Aerobic Biological Treatment

Because of the apparent toxicity of the groundwater to a biological treatment system and the rapid breakthrough of TOC in adsorption systems, it was decided to

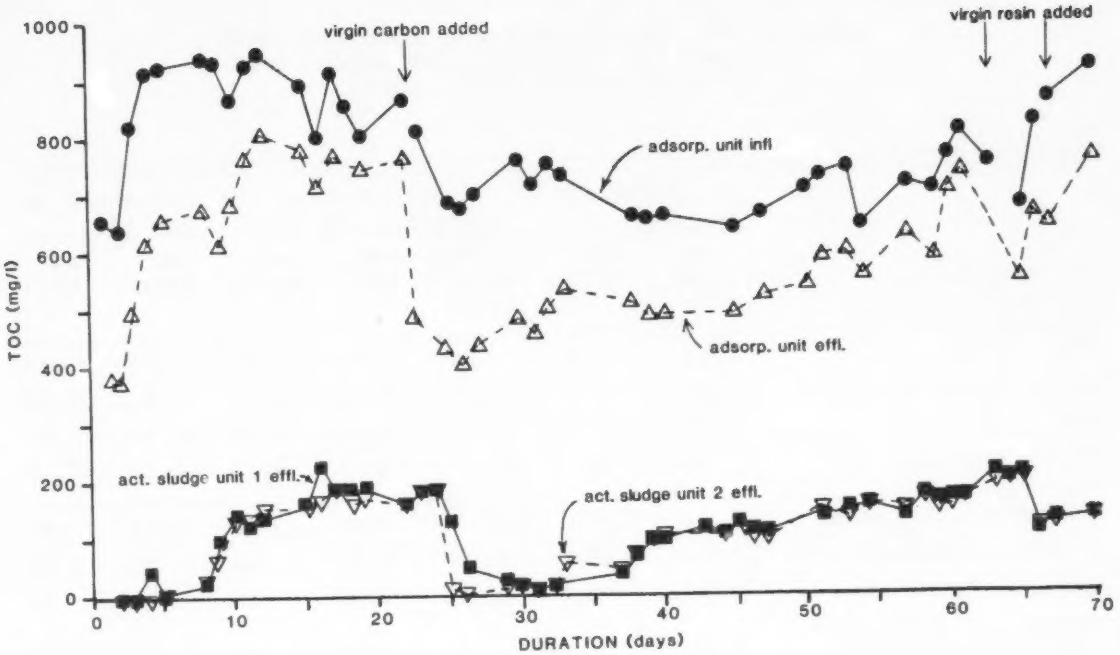


Figure 3. Performance of adsorption/activated sludge process

200 mg/l TOC at this time.

As shown in Table 3, limited analyses made during operation of the GAC/AS train suggest that high levels of organic priority pollutant removals can be attained even with effluent TOC concentrations of 100 to 200 mg/l. Almost all of the organic priority pollutants detected in raw groundwater were removed consistently to less than the level of detection (0.01 mg/l) by the process train. One consistent feature of these data and previous GC/MS analyses from batch carbon adsorption studies is the early leakage of 1,2-dichloroethane. A few other compounds (benzene, methylene chloride, and toluene) also were detected to have broken through the carbon in some batch and continuous flow studies. Acid and base-neutral extractable compounds generally did not break through the GAC process. Data in Table 3 also indicate that the activated sludge process completely removed the few organic priority pollutants leaking through the GAC system even though TOC removal declined. The continued removal of organic priority pollutants may be due to stripping.

An effort was made to determine if specific organic priority pollutants were concentrated in the biological sludge. In the one sludge sample collected to date, no organic priority pollutants were detected at a 0.01 mg/l detection level.

An off-gas sample from the aerated reactor was collected using a cold trap (acetone and dry ice) to condense off-gas vapors. Air flow to the reactor was approximately 2 l/m and the collection period was 4 hours. The following organic priority pollutants were detected in this sample:

Methylene Chloride	1.02 μg/l air
1,2-Dichloroethane	1.04 μg/l air
Benzene	0.25 μg/l air
Perchloroethylene	0.125 μg/l air
Toluene	0.088 μg/l air

TABLE 3. TOC AND PRIORITY POLLUTANT DATA FOR GRANULAR ACTIVATED CARBON/ACTIVATED SLUDGE PROCESS TRAIN (mg/l)

	Collected on Day 2*		Collected on Days 9 and 10			Collected on Day 17	
Compound	Raw Ground-water	GAC Effl.	Raw Ground-water	GAC Effl.	As Effl.	GAC Effl.	AS Effl.
TOC	637	380	929	604	90	770	183
Total Cyanide	NA	NA	0.11	0.21	0.23	0.23	0.20
CN_A	NA	NA	<0.05	<0.05	<0.05	<0.05	<0.05
Total Phenol	NA	NA	16	<0.16	<0.10	<0.10	<0.10
Methylene chloride	2.1	0.029	14	0.01	ND	0.16	ND
1,1-Dichloroethene	1.6	ND	0.06	0.01	ND	ND	ND
1,1-Dichloroethane	2.4	ND	0.17	0.02	ND	ND	ND
Trans-1,2-dichloroethane	0.06	ND	0.04	ND	ND	ND	ND
Chloroform	9.8	ND	0.70	0.06	ND	ND	ND
1,2-Dichloroethane	72	ND	25	1.4	ND	0.05	ND
1,1,1-Trichloroethane	7.6	ND	0.39	0.04	ND	ND	ND
Trichloroethylene	0.06	ND	0.03	ND	ND	ND	ND
Benzene	1.2	ND	1.5	0.02	ND	ND	ND
1,1,2-Trichloroethane	0.11	ND	0.07	ND	ND	ND	ND
Perchloroethylene	0.49	ND	1.9	ND	ND	ND	ND
Toluene	2.3	ND	0.97	0.05	ND	0.01	ND
Chlorobenzene	0.23	ND	0.29	ND	ND	ND	ND
Phenol	0.025	ND	0.028	ND	ND	ND	ND
2-Chlorophenol	0.040	ND	0.036	ND	ND	ND	ND
2,4-Dichlorophenol	0.010	ND	0.010	ND	ND	ND	ND
1,2-Dichlorobenzene	0.085	ND	0.077	ND	ND	ND	ND
Dibutyl phthalate	ND	ND	ND	ND	0.05	ND	ND

NA - Not Analyzed
ND - Not Detected
No other priority pollutants detected at 0.01 mg/l detection limit
* - Refers to Figure 3.

As indicated in Figure 3, on day 64, the pretreatment process was changed from GAC adsorption to resin adsorption (carbonaceous resin XE-347). The operating conditions for two resin adsorption pretreatment studies were as follows:

- 3 columns in series
- columns were 2.54 cm diameter
- total BV = 792 to 835 cm^3
- downflow operation at 41 to 50 ml/min (2.95 t0 3.79 BV/hr)
- EBCT ranged from 20 to 16 min

Results, as shown on Figure 2, indicate that TOC removal diminished to < 50% after ~ 5 BV were loaded and appeared to stabilize at 10-20% for at least 120 BV. The characteristics of the TOC breakthrough curve are similar to those of GAC except that XE-347 TOC removal declined more rapidly.

As shown in Figure 3, the AS units loaded with resin treated groundwater were not able to reduce TOC levels to < 100 mg/l even for a short period after virgin resin was placed on line. Performance at 4 hr and 8 hr HRTs did not differ.

Adsorption/Anaerobic Biological Treatment

With the thought of minimizing potential air pollution due to stripping of volatile organics during biological treatment, an attached-growth upflow anaerobic filter currently is being investigated. The process is preceeded by GAC pretreatment. Operating conditions for the process train are as flows:

- GAC column - 91.4 cm by 2.54 cm ID glass
- GAC influent flow - 1.75 ml/min
- GAC EBCT - 3.8 hr
- UAF column - 70.5 cm by 4.76 cm ID glass
- UAF organic loading rate - 0.423 to 0.847 kg TOC/m^3/d (26.4 to 52.9 lb TOC/1000 ft^3/d)
- UAF EBCT - 13.1 to 22.8 hr
- UAF temperature $35^{\circ}C$

The UAF reactor was filled with ceramic berl saddles and then with sludge from a well operated municipal wastewater sludge anaerobic digester. The UAF reactor initially was fed raw sewage for eight days prior to converting to GAC pretreated groundwater.

Performance data on the GAC/UAF process train are shown in Figure 4. TOC removals by the various steps in the process train are summarized below:

	removal	
	average	range
GAC/UAF train	66%	38-81%
GAC process	31%	10-46%
UAF process	50%	12-67%

Gas production during the initial month of operation has averaged 505 ml/g TOC fed. Figure 4 indicates that UAF effluent TOC increased as TOC leakage from the GAC pretreatment process increased. However, TOC removal and gas production data cannot be related to organic loading rate or other operational data such as sludge pH, sludge total alkalinity, or volatile acids production. In an attempt to bring the pH into a range reported to be most optimal (pH 7.2 to 7.6), the GAC influent pH was adjusted to ~ pH 7.0 to 7.5. This has had no apparent effect on performance. Initial results indicate that about 40% (117 mg/l) of the TOC in UAF effluent can be removed by air stripping.

Recently, this process train was modified by adding activated sludge treatment following the UAF process. A comparison is being made of TOC removal by stripping and biological activity.

Summary

Desktop evaluations of candidate concentration technologies for treatment of hazardous leachates and contaminated groundwater were performed in order to select and priority order technologies for laboratory study. These evaluations were based upon the characteristics of each technology and upon its known effectiveness in concentrating materials in specified chemical classes.

Technologies identified as most promising for experimental study were:

1. adsorption - carbon and resin,
2. biological treatment,
3. biophysical treatment,
4. chemical coagulation,
5. membrane processes - reverse osmosis and ultrafiltration,
6. stripping - air and steam.

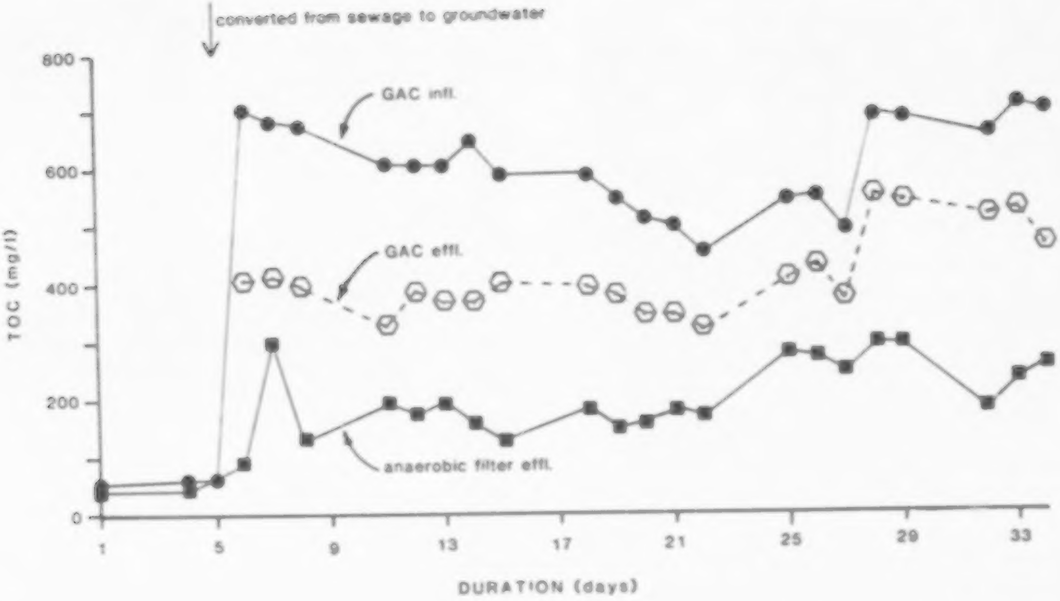


Figure 4. Performance of GAC/UAF process

Subsequently, laboratory experiments on contaminated groundwater at the Ott/Story Chemical Company site in Muskegon, Michigan were initiated. Laboratory results indicate good removals of volatile priority pollutants by batch air stripping. In addition batch carbon and resin sorption reduce all organic priority pollutants by greater than 98%. However, high effluent TOC levels have been measured subsequent to all applied treatments. This TOC represents organic contamination by non-priority pollutants.

Steam stripping in a packed column resulted in concentration of TOC in the overhead condensate stream. However, within the range of feed flow and overhead flow rates investigated, TOC of the bottoms could not be reduced below about 400 mg/l. Overhead TOC approached 4000 mg/l at an overhead flow rate of approximately 6% of the feed flow.

FS 300 granular activated carbon (GAC) employed in continuous flow small size columns was not capable of sustaining high levels of TOC removal. TOC removal declined to < 50% after processing < 5 BV at hydraulic loading rates of ~ 1.85 gpm/ft^2. Within 100-160 BV loaded, TOC removal declined to 10 to 15% and remained at this level for up to 200 BV. GAC adsorption was capable of achieving high levels of organic priority pollutnat removals even when TOC removal had declined to 35% and effluent TOC levels were ~ 600 mg/l. In both batch and continuous flow adsorption studies, some volatile priority pollutants were detected in the effluent. None of the acid or base-neutral extractable organic priority pollutants detected in the raw groundwater were found in GAC effluent after processing up to 71 BV.

Continuous flow small size resin adsorption (XE-347 carbonaceous resin) studies demonstrated TOC breakthrough characteristics similar to those for GAC adsorption. However, TOC breakthrough occurred more rapidly.

GAC pretreatment of raw groundwater permits development of a culture of aerobic organisms capable of further treating GAC effluent. In excess of 95% TOC removal can be achieved by this process during the period which GAC removal of TOC exceeds 30%. After this initial period, process train performance declines as GAC performance declines. Several organic priority pollutants were detected in off-gas from AS reactors; these included methylene chloride, 1,2-dichloroethane, benzene, tetrachloroethylene, and toluene. No organic priority pollutants were detected (at a detection limit of 10 μg/l) in an AS biomass sample.

Anaerobic treatment (upflow anaerobic filter, UAF) of GAC pretreated groundwater is possible. However, UAF performance appears to decline as GAC performance declines (although changes in UAF organic loading rate do not appear to effect UAF performance). Initial results indicate that about 40% of the TOC in UAF effluent can be removed by air stripping. Overall the GAC/UAF process train performs more poorly than the GAC/AS process train with an upper TOC removal limit of 81%. Removal has averaged 66% and ranged from 38 to 81%.

Acknowledgement

The work upon which this paper is based was performed pursuant to Contract No. 68-03-2766 with the Environmental Protection Agency.

The cooperation and assistance of Cordova Chemical Company, the present owner of the Ott/Story site, is greatly appreciated.

References

1. Pajak, A.P., A.J. Shuckrow, J.W. Osheka, and S.C. James. 1980. Concentration of hazardous constituents of contaminated groundwater. In: Proceedings of the Twelfth Mid-Atlantic Industrial Waste Conference. Bucknell University, Lewisburg, Pennsylvania. pp. 82-87.

2. Shuckrow, A.J., A.P. Pajak, and J.W. Osheka. 1980. Concentration Technologies for Hazardous Aqueous Waste Treatment. Interim Report for Contract No. 68-03-2766, U.S. Environmental Protection Agency, Cincinnati, Ohio.

3. Shuckrow, A.J., A.P. Pajak, and C.J. Touhill. 1980. Hazardous waste concentration technologies. In: Treatment of Hazardous Waste, Proceedings of the Sixth Annual Research Symposium. EPA-600/9-80-011, U.S. Environmental Protection Agency, Cincinnati, Ohio. pp. 50-61.

APPLICATION OF REMOTE SENSING TECHNIQUES TO EVALUATE SUBSURFACE CONTAMINATION AND BURIED DRUMS

SHWRD Annual Research Symposium

Harold J. Yaffe
Nancy L. Cichowicz
Robert W. Pease, Jr.
The MITRE Corporation
Bedford, Massachusetts 01730

ABSTRACT

Several remote sensing techniques (ground-penetrating radar, electrical resistivity, metal detection and seismic refraction) were employed to investigate subsurface chemical contamination and buried drums at an uncontrolled hazardous waste site in Rhode Island. The techniques were applied in conjunction with direct sample collection to support the selection of a long-term abatement alternative for the site. The results of the field investigation are given and a comparison of the remote sensing techniques is presented. Recommentations for accomplishing systematic investigations at other abandoned hazardous waste sites are also given.

INTRODUCTION

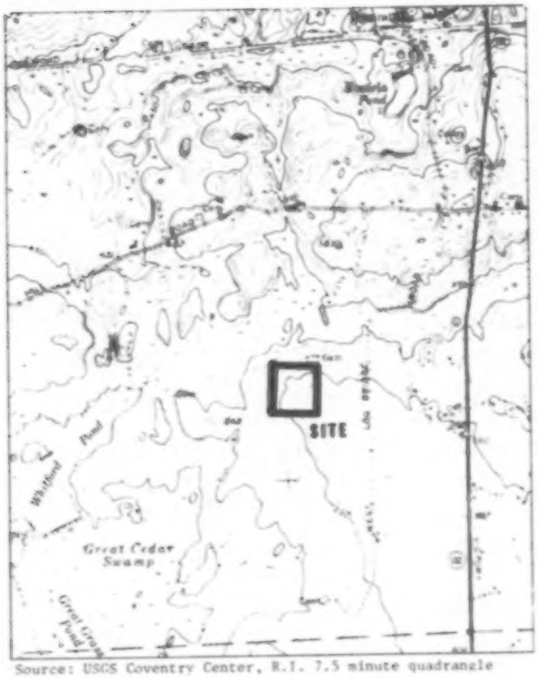
This paper describes the application of several remote sensing techniques in conjunction with direct sample collection at an uncontrolled hazardous waste site to a) determine the extent and nature of the buried drum and subsurface chemical contamination problem and b) support the selection and design of a long-term abatement approach. The use of the following remote sensing techniques were also demonstrated:

- ground-penetrating radar
- electrical resistivity
- seismic refraction
- metal detection.

The focus here is on the techniques and their results as opposed to the selection of the preferred abatement alternative. The latter is discussed in a separate technical report [Cichowicz, et al. (1)].

The uncontrolled hazardous waste dump site which was investigated is located in Coventry, Rhode Island, approximately 20 miles southwest of Providence. The site encompasses approximately 7.5 acres of cleared ground surrounded by woods and wetland in a relatively rural area of the state (see Figure 1). An undetermined quantity of chemicals had been placed into the ground both by the burial of 55-gallon drums in five separate locations and by direct discharge into trenches (see Figure 2). A swamp, located northwest of the site, is the surface discharge area of chemicals leaching from the dump. This swamp discharges to a small pond which is a source of irrigation water for a cranberry bog located approximately one mile from the swamp's outlet. To date, no evidence of chemical contamination in the pond has been found, based on sampling conducted by the Rhode Island Department of Environmental Management (DEM) and the U.S. Environmental Protection Agency (EPA), Region I.

State of Rhode Island officials were alerted to the dumping activities by a fire


SITE
Great Cedar Swamp

Source: USGS Coventry Center, R.I. 7.5 minute quadrangle

Figure 1. Topographic map of the hazardous waste site in Coventry, Rhode Island.

and explosion in September 1977. A court order issued in November 1977 prohibited the property owner from continuing dumping activities or otherwise altering the site. From the end of 1977 to mid-1979, the DEM conducted field investigations to quantify the seriousness of the situation.

In October 1979, the DEM contracted with The MITRE Corporation to conduct a systematic site assessment, and in April 1980 the investigation continued under funding by the EPA/SHWRD. Although the investigation of the Coventry site was conducted in two discrete phases with separate project reports, overall project continuity was maintained. Phase I funding was shared by the DEM and EPA/SHWRD (the latter funded all chemical analysis and the preliminary evaluation of abatement methods) and Phase II was completely undertaken by EPA/SHWRD.

SITE INVESTIGATION

The ultimate purpose of the Phase I and Phase II investigations was to support the selection of one of the following long-term abatement methods:

- site encapsulation
- leachate collection and treatment
- drum removal and chemical disposal

or the "no action" alternative.

The techniques employed for data collection during the Phase I effort were: electrical resistivity; metal detection; installation of monitoring wells; and chemical analysis of soil, ground water, and surface water. The field methods employed, data collected, conclusions drawn, and recommendations made to the DEM are documented in the Phase I project report [Pease, et al. (3)]. Although the extent of the problem was defined and abatement options were preliminarily evaluated, certain key pieces of information (concerning the presence of fracturing or contamination of the bedrock and the condition and number of the buried drums) needed to be ascertained before a

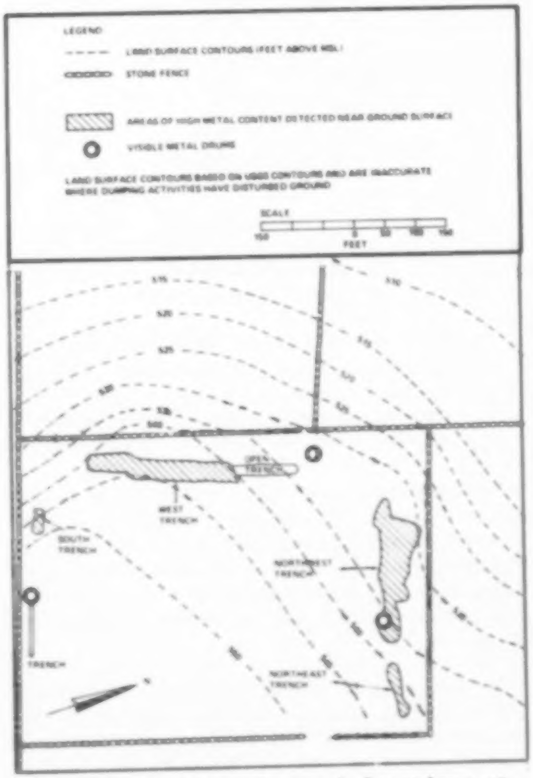

LEGEND
LAND SURFACE CONTOURS (FEET ABOVE MSL)
STONE FENCE
AREAS OF HIGH METAL CONTENT DETECTED NEAR GROUND SURFACE
VISIBLE METAL DRUMS
LAND SURFACE CONTOURS BASED ON USGS CONTOURS AND ARE INACCURATE WHERE DUMPING ACTIVITIES HAVE DISTURBED GROUND
SCALE
FEET
OPEN TRENCH
WEST TRENCH
SOUTH TRENCH
NORTHWEST TRENCH
NORTHEAST TRENCH
TRENCH

Figure 2. Outline of trench locations at the Coventry site as determined by metal detection.

TABLE 1. TECHNIQUES USED IN PHASE II TO PROVIDE INFORMATION NEEDED TO SELECT AN ABATEMENT ALTERNATIVE

Alternative	Additional Information Required to Select Alternative	Technique to Obtain Information*
1. No Action	• condition of source (drums) • state of nearby pond • contaminant underflow at swamp • ultimate disposition of all pollutants	• radar, exploratory excavation • additional wells, chemical analysis of soils and water samples
2. Drum Removal and Disposal (excavation, testing, and proper disposal of drums and contents, and contaminated soils)	• condition of source (drums) • condition of soil	• radar, exploratory excavation • exploratory excavation, chemical analysis of soil samples
3. Site Encapsulation (construction of impermeable barriers around source of pollutants)	• condition of source (drums) • condition of bedrock	• radar, exploratory excavation • seismic refraction, core drilling, deep wells
4. Leachate Collection and Treatment		
a. Limited Option (interceptor trenches constructed adjacent to site walls)	• condition of source (drums) • condition of bedrock	• radar, exploratory excavation • seismic refraction, core drilling, deep wells
b. More Complete Option (interceptor trenches constructed 600 feet downgradient of site walls)	• same as above	• same as above

*Metal detection had previously been used to locate trenches; electrical resistivity to delineate leachate plume. Radar could have been employed in lieu of or in conjunction with metal detection, as recommended for other sites; potential radar effectiveness was not known at the time of the initial survey.

permanent solution could be selected. The Phase I report presented the abatement options, identified the necessary additional information, and made recommendations for immediate and near-term actions to protect the public health and to collect additional data.

The relationships among the abatement methods, the additional information needs at the conclusion of the Phase I study, and the techniques employed in Phase II to obtain that information are shown in Table 1. Phase II was undertaken by MITRE with EPA/SHWRD funding (ground-penetrating radar, seismic refraction, bedrock sampling, and chemical analysis) and by the DEM under internal state funding (exploratory excavation of one trench). A project report [Cichowicz, et al. (2)] which describes the use and evaluation of the remote sensing techniques, and a supplementary project report [Cichowicz, et al. (1)] which describes the evaluation of abatement alternatives are currently being published by EPA/SHWRD.

REMOTE SENSING TECHNIQUES

Ground-Penetrating Radar

The technique of ground-penetrating radar involves the repetitive propagation of short-time duration pulses of electromagnetic energy in the radio frequency range downward into the ground from a broad bandwidth antenna on (within a few inches of) the surface. Reflections from subsurface interfaces are received by the antenna during the off period of the pulsed transmission, processed electronically, and recorded to yield a continuous profile of subsurface conditions as the antenna/transmitter-receiver unit is moved across the ground surface. The depth d to an interface, or the surface of a "target" such as a metal drum, is calculated from $d = (vt)/2$, where v is the wave velocity (equal to $c/\sqrt{\epsilon_r}$, where c is the velocity of light and ϵ_r is the relative dielectric constant of the material in which the wave is propagating) and t is the pulse travel time.

Ground-penetrating radar has been used in such applications as archeological surveys, locating sewer lines and buried cables prior to construction activities, and profiling lake and river bottoms. The application to locating buried drums of chemical wastes is relatively new, and further refinements both in the technology and in data interpretation are anticipated.

The field survey was conducted by the equipment manufacturer, Geophysical Survey Systems, Inc. (GSSI). The equipment used was GSSI's Surface Interface Radar System 7. The survey of the trench areas, representing approximately two acres, took two days. Following experimentation with two alternative antennas and center frequencies, GSSI Model 3105AP operating at a center frequency of 300 MHz and GSSI Model 3102 operating at 600 MHz, the latter was chosen for most of the survey due to its improved spatial resolution at shallower depths. The operating depth varies approximately as the inverse square of the frequency, all else being equal.

One large trench (labeled the West Trench in Figure 2) located by the metal detection survey was surveyed with the 300 MHz antenna set at a nominal depth of 25 feet, later calibrated at 24.4 feet, based on average soil conditions. The other trenches (labeled Northwest, Northeast, and South) were subsequently surveyed using the 600 MHz antenna set at a nominal depth of 12.5 feet. The survey was conducted according to a rectangular grid. All trenches were surveyed longitudinally by using parallel radar transects at spacings of ten feet. Transverse transects, or cross-cuts, were made at intervals of 20 feet for the Northeast Trench and 40 feet for the West and Northwest Trenches. The antenna unit was pulled along each transect manually, and the data recorded by wire connection with equipment located in a stationary van on the site, which also served as the power source. The major equipment components were a control unit with cathode ray tube display, a tape recorder, a graphic (chart) recorder, and a solid state inverter.

The radar beam has a spread of ±45° in the fore and aft directions, and ±20° laterally. Any target detected within this beam will be recorded as being directly below the point of the surface where the signal is transmitted and received, and signals are reflected only from surfaces perpendicular to the direction of the signal. The use of a 10-foot grid spacing thus resulted in a sampling approach, as opposed to full coverage of the subsurface volume. However, even with a very fine grid, a fraction of the buried drums would be missed by the radar due to a) their orientation or b) their being "shielded" by metal drums closer to the surface, since metal is a near-perfect reflector of radar energy.

Illustrative data from the survey are shown in Figures 3, 4, and 5. The ground surface is at the top of each figure whereas the bottom of the figure corresponds to a depth of approximately 12 feet. The vertical dashed lines are markers produced electronically in the field, which correspond to 10-foot intervals. Figure 3 illustrates a subsurface profile where there are no buried drums. This profile was taken over an area of undisturbed soil.

In Figure 4, there are a number of individual targets identifiable by the characteristic hyperbolic "signature". This signature results from the increased travel time between the target and the antenna when the beam approaches or moves away from the target versus when it is directly over the target. Each reflecting target will produce three characteristic hyperbolas. It is possible for a skilled interpreter to distinguish between the signature caused by a drum or boulder either in the field or from the recorded data. In the field, a metal object can be determined instrumentally by comparing the polarity of the target signal to the background signal. A metal object which is essentially a perfect reflector, will produce a signal that is "in phase" with background. An object such as a boulder will produce a signal reversed from background. Close examination of the recorded data will also show another reflecting signal produced by a metal object in addition to the three characteristic hyperbolas. The fourth image found above the characteristic three is also caused by the reflection from metal and would not be present on the data if the target were a boulder.

Figure 5 shows a blurred effect which is interpreted as being caused by a concentration of contaminants, as from a leaking drum. Chemical analysis by the DEM has shown that some of the chemicals being released from the drums are ionic, which is a characteristic that would increase the attenuation of the radar signal strength. Therefore a noticeable blurred contrast relative to the average strength is observed on data taken over a trench containing a high concentration of contamination.

Metal Detection

The entire 7.5 acre site in Coventry was surveyed by personnel from Fred C. Hart and Associates, Inc. with a Fisher M-Scope (Model TW-5) metal detector. This equipment is designed for locating buried metal objects by inducing an electromagnetic field around the object in response to radiation from a transmitter. The average depth of detection for metal objects is dependent on the amount of background "noise". Thus in areas free of buried metal, the probable depth of detection was approximately six to eight feet. In areas of buried drums, the sensitivity setting of the instrument had to be cut back, resulting in a potential

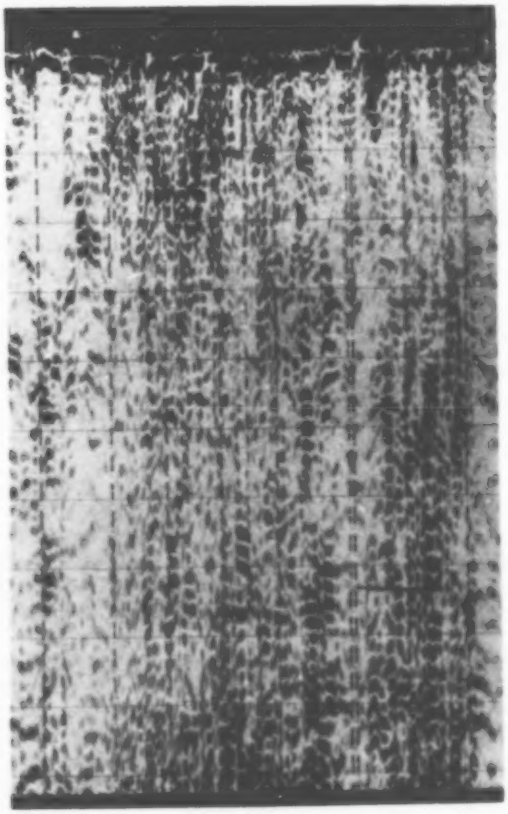


Figure 3. Radar profile taken outside trench boundary.

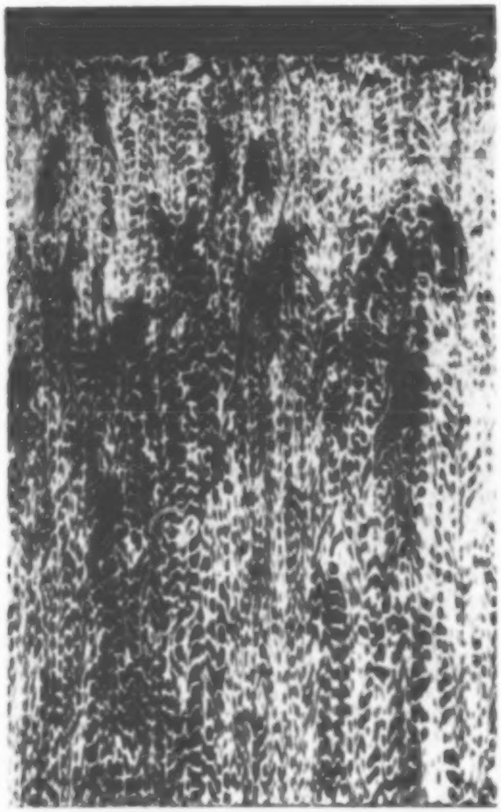


Figure 4. Radar profile taken within trench boundary showing "signature" of buried drums.

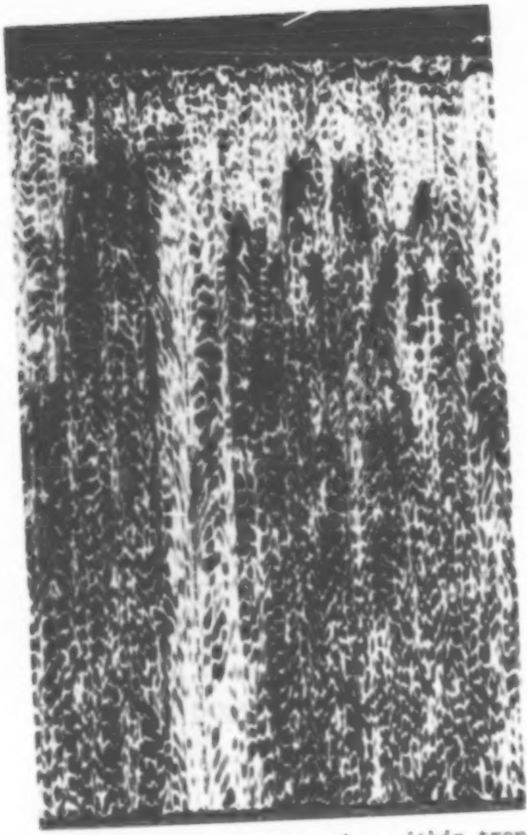


Figure 5. Radar profile taken within trench boundary showing buried drums and chemical contamination (blurriness near center of photo).

depth of metal detection of approximately four to five feet. In areas where buried drums were suspected, based on disturbed ground or the initial gross scan of the overall site, the survey was conducted by traversing closely-spaced grid lines.

Electrical Resistivity

The electrical resistivity of a geological formation depends upon the conduction of electric current through the particular subsurface materials. Since most of the geologic formations that contain water have high resistivities, the electrical resistivity of a saturated rock or soil is primarily a function of the density and porosity of the material and the concentration of the conducting ions within the saturating fluid. In a resistivity survey, an electric current is passed into the ground through a pair of current electrodes and the potential drop is measured across an inner pair of potential electrodes. The "apparent resistivity" is determined by the equation, $R_a = 2\pi A(V/I)$, where A is the electrode spacing, V is the potential difference, and I is the applied current. The depth of penetration is controlled by the distance between the electrodes (called the A-spacing) and is approximately equal to half of this distance. Varying the A-spacing allows resistivity measurements to be taken in the form of either lateral or depth profiling.

Both types of profiling methods were conducted at the hazardous waste site in Coventry using a Bison Instruments Model 2350B Earth Resistivity meter powered by a 90-volt battery. A fixed electrode spacing of 20 feet was used for the lateral profiles in the areas of the trenches and the swamp where the depth of ground water contamination was suspected as being shallow. Two lateral profiles using a fixed A-spacing of 50 feet were also conducted approximately 2000 feet west and north of the immediate site walls, where it was suspected that the contamination might be detected at greater depths.

Additionally, seven depth profiles were conducted in the vicinity of the West Trench located previously by the metal detection survey. Electrodes were set at intervals of 1, 2, 4, 8, 16, and 32 feet at each profile location, permitting a maximum depth of investigation of approximately 15 feet. Resistivity readings were taken at each spacing interval for the left, right, and central spacings. This particular spacing interval was chosen based upon the intents of the investigation, which were to identify changes in subsurface contamination and to locate the boundary defining the bottom of the trench. The lateral surveys were conducted by Fred C. Hart and Associates, Inc. and the vertical surveys by Stephen A. Alsup and Associates, Inc.

Seismic Refraction

The seismic refraction method is based on the principal that elastic waves (mechanical rather than electromagnetic) travel through different subsurface strata at different velocities. Elastic waves are introduced to the ground surface by an energy source, usually a small explosion or a hammer blow on a steel plate for shallow investigations. The refracted waves are detected by small seismometers (geophones) located on the surface at various distances from the energy source. A seismograph records the travel time between the vibration and the arrival of the elastic wave at the geophones. Plotting arrival time versus distance from the energy source to geophone from a series of seismograph records enables the determination of strata depths and their seismic velocities through the use of simple refraction theory.

Seismic refraction profiling of approximately 2,850 linear feet was performed at the Coventry site in two days of field work by Stephen A. Alsup and Associates, Inc. A Geometrics/Nimbus Model ES1210F Multichannel Seismograph was used to record and collect the voltage outputs from 12 geophones spaced at 20-foot intervals for each refraction spread. The energy source used to initiate each record and shock wave was a 30-pound weight drop or 10-pound sledge hammer blow on a steel plate with an attached impact start switch.

The seismograph, which includes a digital memory of waveform from each data channel, allows repetitions of the elastic waves from a series of hammer blows thereby enhancing the ability to detect signals and pick arrival times. The use of the hammer drop as the energy source (which is preferable to using small explosive charges in this type of investigation) would be more difficult without the digital memory of the seismograph. Impact points for this survey were at the end of, and quarterly along, the refraction spread, providing a locus of depth calculations at 80-foot intervals along each spread. Data continuity and repetition were achieved by repeating end shots where refraction lines were longer than one spread length.

RESULTS OF FIELD STUDIES

Plume Delineation

Having determined the information needed to evaluate the long-term abatement alternatives, the Phase I investigation was planned. A principal component of the site investigation was the installation of shallow monitoring wells in order to collect soil and water samples and to determine ground water elevations.

Because natural conditions at the site were such that measurement of electrical resistivity was expected to be successful, a lateral profiling survey was performed to facilitate the placement of monitoring wells. In addition, a depth profiling survey was conducted to determine vertical contamination patterns. Figure 6 shows the apparent resistivity values obtained during the lateral profiling survey, plotted on a contour map. The measurements taken using both the 20- and 50-foot A-spacing are given. Rather than showing that the plume was moving directly toward the swamp in a northwesterly direction as suspected from measurement of water levels in existing monitoring wells, the apparent resistivity values gave an indication of two distinct plumes (a western and a northern plume) at different depths with each having a separate source. With increasing distance from the site, however, the two plumes joined finally to discharge in the swamp.

The western plume, which was defined primarily using the 20-foot A-spacing, appears to be generally within 10 feet of the surface. Most of the plume moving toward the north was defined using the 50-foot A-spacing and appears generally deeper than 20 feet below the surface. However, some shallow contamination is also apparent along the northern border of the site near the trenches. Shallow bedrock off the northwest corner of the site was considered the most likely explanation for the high apparent resistivity values between the two plumes, although this explanation was later proven to be false (see next subsection). Hence, the results of the resistivity survey suggest that additional monitoring wells be located to determine the existence of the shallow bedrock and to substantiate the presence of two separate plumes.

Additionally, a discovery of a contaminant source along the partly grass-covered western edge of the site was important information, since it served to indicate how far south and west the monitoring well program ideally should extend. Locating this additional source of contamination may also have been possible using the radar technique based upon comparison of signal strength.

As previously mentioned, several depth profiling resistivity surveys were conducted in the vicinity of the West Trench to determine vertical changes in contamination. Figure 7 is a plot of the apparent resistivity versus approximate depth below the surface for several profiles taken over and outside of the trench boundary. Presentation of the data in this manner allows comparison of the "normal" or background resistivity patterns observed outside the West Trench where no contamination is expected, to the patterns observed over and downgradient from the trench where the occurrence of contamination is anticipated.

Profiles 1 and 6, taken outside the major plume boundary, as indicated by the lateral resistivity survey, are indicative of background patterns. Profile 2 was taken in the open, unfilled trench where no drums were buried, but bulk chemicals were suspected to have been discharged. This profile shows the effect of free-standing water in the trench and perhaps some slight contamination within the first few feet of the surface, and then an increase in resistivity to near background conditions. This indicates that either the open trench was not used for bulk dumping of significant amounts of chemicals with high electrical conductivity (since conductive effects decrease rapidly below several feet of depth), or that significant portions of the chemicals have been removed by leaching. Profiles 3, 4, 5, and 7, taken over or downgradient from the West Trench, show the varying degrees of contamination within the plume. A very high contentration of drums may explain the extremely low resistivity measured at the location of profile 4. The volume of highly conductive chemicals at this location is inferred as being very large in order to have such a strong effect on the resistivity measurements. A very localized concentration of conductive chemicals would not be expected to have such a strong effect with this particularly wide electrode spacing (32 feet).

Figure 8 shows the same seven profiles, but on a plot of "cumulative" resistivity versus approximate depth below the surface. Slope changes or breaks in the cumulative curves generally indicate the depth of the underlying unit, and the direction of slope change indicates the relative resistivity

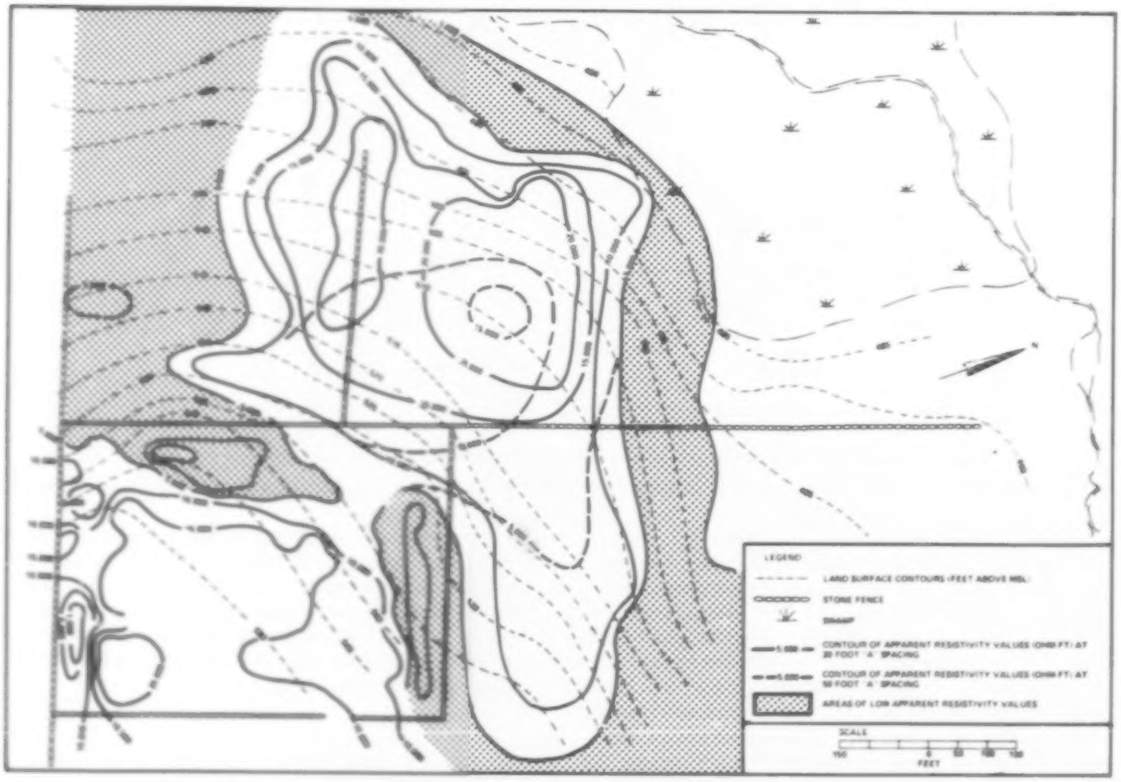

LEGEND
LAND SURFACE CONTOURS (FEET ABOVE MSL)
STONE FENCE
SWAMP
CONTOUR OF APPARENT RESISTIVITY VALUES (OHM FT) AT 20 FOOT "A" SPACING
CONTOUR OF APPARENT RESISTIVITY VALUES (OHM FT) AT 50 FOOT "A" SPACING
AREAS OF LOW APPARENT RESISTIVITY VALUES
SCALE
FEET

Figure 6. Contour map of apparent resistivity values.

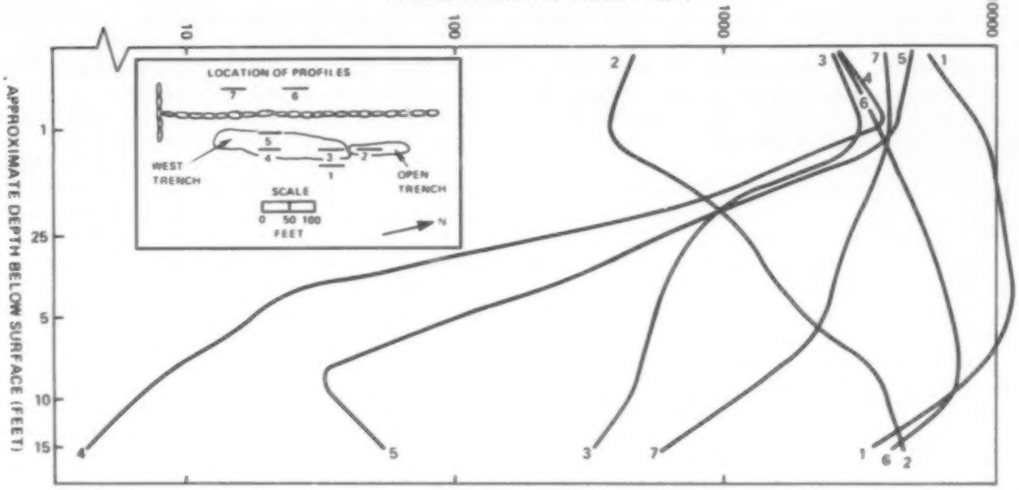


Figure 7. Apparent resistivity depth profiles for several locations near the West Trench.

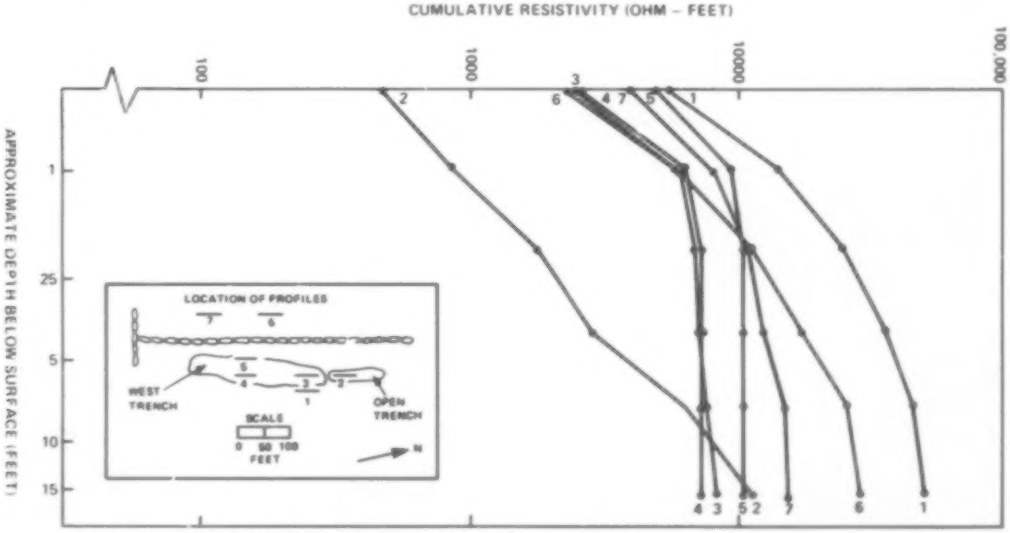


Figure 8. Cumulative resistivity depth profiles for several locations near the West Trench.

values of the subsurface materials. Thus, an increasing slope signifies that the underlying unit has a higher relative resistivity, whereby a decreasing slope denotes a lower relative resistivity in the underlying unit. In accordance with the interpretation of Figure 7, Figure 8 shows higher relative resistivities with depth (no contamination) for profiles 1 and 6. Interpretation of profile 2 is more straightforward using the cumulative resistivity plot. Slight decreases in slope, denoting lower resistivity or presence of soil moisture or contamination, are evident between two and five feet and below ten feet. Profiles 3, 4, 5, and 7 show a continued decrease in slope with depth, which is expected because of their locations within the buried drum area or downgradient from the trench.

Determination of the depth of the bottom of the West Trench was not possible using the vertical resistivity plots. It is not clear, however, whether the particular A-spacing used for these profiles (32 feet) was wide enough to allow adequate penetration necessary to detect the bottom of the trench. A second possibility is that there is no detectable change in contamination at the bottom of the trench thereby causing a continuation of the low resistivity readings beyond the region of buried drums.

Fifteen monitoring wells were installed following the lateral resistivity survey. Refusal depths, tentatively assumed to reflect the approximate top of bedrock, did indicate a mound in the bedrock surface off the northwest corner of the site. Four wells in this vicinity were dry, which also gave credence to the results obtained from the resistivity survey, namely the existence and location of two plumes. In addition, soil samples taken from these same locations were much less contaminated than soil samples taken from borings located within the plume boundaries. Consideration of these factors seemed to indicate that ground water flow was being diverted around a bedrock mound and this had resulted in the detection of high apparent resistivity values in this area. It was found by subsequent (Phase II) bedrock drilling, seismic refraction survey, and chemical analysis of soil and ground water that the bedrock mound did not exist and that contaminated ground water was indeed traveling in this location. In general, the ground water is at a greater depth below the surface in this region than the other surveyed areas, thus resulting in higher relative resistivity values, and subsequent incorrect interpretation.

Determination of Bedrock Topography

Complete verification of the shallow bedrock off the northwest corner of the site was not possible until the bedrock coring and the seismic survey were performed. The drilling showed that the refusal depths of the previous borings had actually been due to boulders and/or very dense till. At each boring location, the bedrock (a granite gneiss) was discovered to be 10 to 30 feet deeper than anticipated. The seismic survey indicated that the bedrock surface was gently rolling, varying from approximately 10 feet below ground surface near the swamp to approximately 70 feet below ground surface on top of the site.

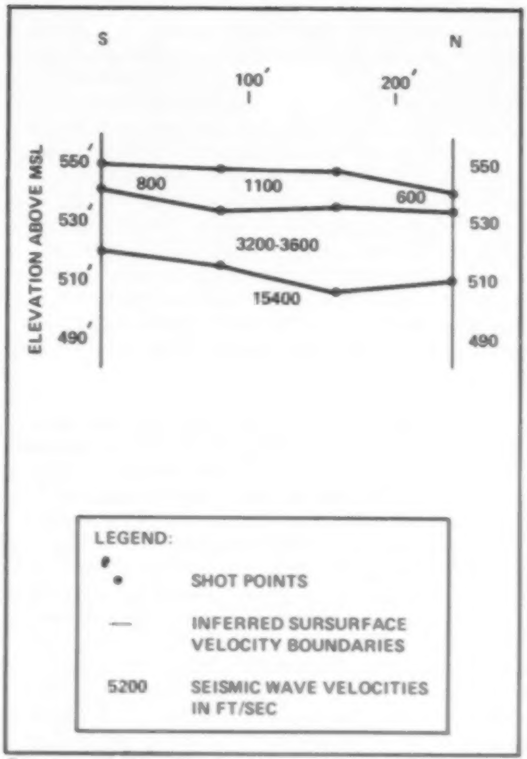
The boring drilled in the area between the two plumes showed that the bedrock was highly weathered and fractured. A piezometer installed in the fractured bedrock indicates that the granite gneiss is hydraulically connected to the unconsolidated glacial deposits. Therefore, ground water is not being diverted around a shallow bedrock mound as had been inferred from the resistivity survey and Phase I drilling, but is actually moving over this area toward the swamp at depths greater than 20 feet. A ground water sample taken from this well was found to contain a diverse assortment of volatile organic pollutants similar in concentration to samples taken from wells within the two plumes.

A seismic refraction profile was performed over the West Trench in an experimental attempt to determine the depth of the base of the buried drums. Neither ground-penetrating radar nor metal detection was able to show the lower boundary of drums and resistivity depth profiles revealed no readily-interpretable trends. Knowing the depth of trenches is critical to the estimation of the number of drums in each trench. A remote sensing method that can effectively determine depth of drums would greatly aid other similar investigations for the determination of drum number and cost estimates of abatement techniques.

The results of the seismic profile of the West Trench are shown by Figure 9. Three distinct velocity units are shown on the profile and it is believed that the upper one, varying from 7 to 14 feet, represents the disturbed soil surrounding the buried drums. However, this interpretation needs to be confirmed through test drilling and/or excavation.

Buried Drum Location and Number

The location and dimensions of the trenches used to estimate the number of drums in each trench were based on a combination of data from metal detection, ground-penetrating radar, and the exploratory excavation. The results from the seismic profiling of the West Trench were used to estimate the lower limit for the bottom of the trenches, even though these data have not been confirmed. For the purposes of estimating the number of drums contained in the trenches, the angle of the vertical side walls was assumed to be 60°, the angle of the declining surface of drums 45°, and the angle of descent of the trench ends 45°. The angle of repose for disturbed site soil



Source: S.A. Alsup and Assoc., Inc.

Figure 9. Subsurface profile of the West Trench as determined by seismic refraction.

is approximately 45°, but excavated side walls were shown to maintain a steeper slope.

Since the radar probed to a depth of 12 feet in contrast with the four to six feet in the vicinity of the trenches for metal detection, the radar would be expected to present a somewhat more accurate indication of trench boundaries. The radar found two trenches in the "Northeast Trench", versus the single trench identified previously with metal detection; the explanation for this is not known. On the other hand, the radar data for the West Trench had to be supplemented by data from the metal detection.

The radar provided, in addition, some useful qualitative information on the way drums were placed and on the trench construction. For example, although there were isolated instances where drums appeared to be neatly stacked, this was the exception rather than the rule; the drums for the most part appeared to be randomly stacked based on the radar data, and at least in the top eight or so feet below the surface (where individual drums most clearly could be identified) the drums appeared to be present in clusters as opposed to being uniformly dense throughout a trench. Also, the top surface of the drums displayed an "angle of repose" from the sides to the center of the trench cross-section.

The radar was not able to detect the bottom of the trenches, partly because the upper drums masked what was beneath. Even in the West Trench, where a 25-foot nominal depth was probed, the trench bottom could not be located from the data. The radar data can often be used, however, to determine the interface between the sides of the trenches and the undisturbed soil. Radar signals from within the trench are generally stronger than signals from outside the trench. This contrast is attributed to the fact that the disturbed soil within the trench has a higher dielectric constant because it is more porous and has a greater moisture content than undisturbed soil. For future work at other sites, it is suggested that deep radar probing at and just outside a trench boundary may be successful in determining the maximum depth of drums, depending on the steepness of the side of the trench relative to the radar beam, the clarity of the radar signal at this depth, and the subsurface material at the given site.

In order to produce estimates for the number of drums remaining buried, a theoretical trench geometry described earlier was employed. It is also assumed for the purpose of the drum estimates that a two-foot layer of soil covered the top of the burial area and two nominal trench depths of 14 and 22 feet were used in order to bracket the range determined from remote sensing and direct excavation. The bottom of the trenches are assumed to be level with no irregularities. Straight sides for the horizontal widths and lengths have also been assumed.

Two densities of drums (percent of volume of drums within trench volume below the cover layer of soil) were used for the drum number estimates: 90 percent and 50 percent. A drum density of 90 percent represents the closest packing arrangement possible for cylinders without regard to interferences imposed by the actual geometry of the trench boundaries. An actual drum density of 54 percent was calculated for the Northeast Trenches using the results obtained from the DEM site representative combined with the theoretical trench geometry. The calculated 54 percent density was rounded off to 50 percent for the lower limit calculations of the drum number estimates.

The estimated range of the number of drums remaining buried at the Coventry site is found in Table 2. The drum estimate was performed by calculating the volume of each trench and multiplying the volume by the assumed drum density to yield the total volume of drums. The estimate for the number of whole drums is provided by dividing the total volume by the volume of a single drum ($7.35\ ft^3$). As Table 2 shows, the overall range varies by a factor of two and a half, from 16,700 to 44,700, while the more likely range based upon the observed depth of the Northeast Trenches is less than a factor of of two, from 25,000 to 44,700.

The above estimates are for whole, uncrushed 55-gallon drums. The numbers will necessarily increase if some are crushed, enabling closer packing. The drum number estimates can be corrected for the presence of crushed drums by multiplying by $g/(f + g - gf)$, in which f represents the fraction of crushed drums and g is equal to the ratio of the volume of a whole drum to the volume of a crushed drum. If $g = 2$ and $f = 0.3$, for example, as indicated by the exploratory excavation of the Northeast Trenches, there would be 18 percent more drums (whole plus crushed); however, there would be 17 percent fewer whole drums.

Prior to the radar survey, an estimated range of drums was made which was substantially lower than the estimates presented here. The earlier analysis plausibly assumed that the trenches with buried drums were of similar construction to that of an unfilled trench on the site. As a lesson for other similar sites, it is wise to keep in mind that without the benefit of more accurate information, the "worst case" corresponds to a steep sided trench (with angle of repose depending on local soils as well as the method of trench construction) with depth approximately equal to the water table, to bedrock, or to the maximum feasible excavation depth.

TABLE 2. ESTIMATED NUMBER OF BURIED DRUMS
BASED ON EXTRAPOLATION OF BEST AVAILABLE DATA

Trench Location	Maximum Drum Density		Drums Randomly Stacked	
	d = 14 ft	d = 22 ft	d = 14 ft	d = 22 ft
Northwest	14,800	22,400	8,200	12,400
West	13,500	20,200	7,500	11,200
South	1,700	2,100	1,000	1,200
Total	30,000	44,700	16,700	25,000

Notes: d = nominal trench depth

Random stacking indicated by results of excavation of Northeast Trenches, approximated by 50 percent drums, earth by volume in trench below 2 ft cover and assumed trench geometry, as described in the text.

Drums are assumed to be uncrushed, 55-gallon drums.

CONCLUSIONS AND RECOMMENDATIONS

Uncontrolled or abandoned hazardous waste sites present varying degrees of difficulty to investigators. For example, abandoned sites which are extensive in area, rural (with hindering vegetation), or in areas of complex geology and hydrology, represent troublesome environments for investigation. Therefore it is important to develop approaches for thorough, but rapid and cost-effective assessments of these difficult situations. In most cases, a well designed and executed investigative program will include remote sensing techniques in addition to direct measurement. Premature action to drill wells, collect and analyze various air, water, and soil samples, or perform excavation without careful planning and proper integration of available techniques may result in unnecessary adverse exposure to hazardous conditions and in an inaccurate or incomplete understanding of the total problem.

Remote sensing techniques may be used to provide reasonably accurate assessments of subsurface contamination, the location and extent of buried drums, and other data needs for determining appropriate methods of abatement. It must be stressed, however, that not all critical information can be obtained remotely, since each of the techniques has limitations, both theoretical and site-specific, and consequently that direct sampling should be undertaken at every uncontrolled hazardous waste site.

Table 3 summarizes the purpose, advantages, and limitations of each of the four remote sensing methods used at the Coventry site. It is important that this type of information be consulted prior to development of an investigatory program. Even though

TABLE 3. COMPARISON OF REMOTE SENSING TECHNIQUES

Technique	Purpose	Advantages	Limitations
Electrical Resistivity			
Lateral Profiling	• determine lateral extent of contaminated ground water • facilitate placement of monitoring wells and optimize their number • monitor changes in plume position and direction	• procedure less expensive than drilling • procedure more rapid than drilling • equipment light-weight, able to be hand carried • survey may be conducted in vegetated areas	• limited ability to detect non-conductive pollutants • technique unsuitable if no sharp contrast between contaminated and natural ground water • interpretation difficult if water table is deep • interpretation difficult if lateral variations in stratigraphy exist • interpretation difficult if radical changes in topography are not accounted for in choice of A-spacing • technique unsuitable in paved areas or areas of buried conductive objects
Depth Profiling	• indicate change in contamination with depth • establish vertical control in areas of complex stratigraphy	same as above	same as above
Seismic Refraction (Non-explosive Method)	• determine depth and topography of bedrock • determine depth of trench containing buried drums	• procedure less expensive than coring or excavation • procedure more rapid than coring or excavation • survey may be conducted in vegetated areas	• technique unsuitable if no sharp velocity contrast between units of interest (e.g., trench containing buried drums and surrounding soil) • survey requires access road for vehicle • depth of penetration varies with strength of energy source • low velocity unit obscured by overlying high velocity units • interpretation difficult in regions of complex stratigraphy
Metal Detection	• locate areas of high metal content (e.g., buried drums)	• procedure less expensive than excavation or radar • procedure more rapid than excavation or radar • equipment light-weight, able to be hand-carried • survey may be conducted in vegetated areas	• technique unsuitable for the detection of non-metallic objects • technique unsuitable for objects below five feet • technique unsuitable for determination of number or arrangement of buried objects
Ground-Penetrating Radar	• locate buried objects (e.g., buried drums) • provide qualitative information regarding drum density • detect interfaces between disturbed and undisturbed soil (e.g., bottom of trenches) • detect plumes of high chemical concentration	• procedure less expensive than excavation • procedure more rapid than excavation • procedure deeper-penetrating than metal detection • procedure yields more information than metal detection • procedure may be used over paved areas	• technique unsuitable for vegetated areas • data requires sophisticated interpretation • underlying objects obscured by those above • survey requires access road for vehicle

there are disadvantages inherent to each technique, proper sequencing and phased studies can potentially result in an overall optimized approach. It must be emphasized that as the study progresses, preliminary conclusions will necessarily be modified and the nature of direct sampling activities will need to be evaluated continuously. It is recommended that final conclusions not be drawn solely from the results of remote sensing methods.

To accomplish site investigations in the most efficient manner, a systematic approach is necessary to take advantage of the information that can be extracted from remote sensing methods. In addition, a systematic approach allows a reduction in the time and cost, and an increase in the effectiveness of direct sampling.

In general, the following two objectives must be addressed by all investigations at uncontrolled hazardous waste sites:

- determination of the nature and extent of the problem and the resulting effects on public health and the environment (both actual and potential)
- determination of environmentally sound and cost-effective methods to effectively abate the problem (if abatement is deemed necessary).

The first activity of an investigation should be identification of specific data needed to meet each objective. After this has been accomplished, the various techniques available for data acquisition, both remote and direct, can be evaluated with regard to the type of information that can be obtained from each in relation to the specific conditions at the site. Although not always the case, it may be reasonably assumed that remote sensing techniques should be used in advance of the more direct data acquisition methods of borings or excavations. This is not intended to imply, however, that all direct sampling should be held in abeyance. There have been numerous instances in which emergency action is dependent upon immediate results from air, water, and soil sampling, and for such cases remote sensing techniques should be used secondarily.

Both the selection and sequence of remote sensing and direct data collection techniques should be determined based upon the specific needs and circumstances of the given site. Additionally, the limitations of the remote sensing techniques presented in Table 3 should be kept in mind. Even the best combination of results obtained remotely provides only an approximate representation of subsurface condition. Finally, since the cost of such site surveys tends to be only a very small fraction of the total cost of ultimate solutions, it is generally cost-effective to apply several overlapping techniques at a site to complement one another and refine the results to support implementation of the preferred long-term solution.

ACKNOWLEDGMENTS

The work on which this paper is based was supported under MITRE contracts with U.S. Environmental Protection Agency (EPA), Solid and Hazardous Waste Research Division, and the State of Rhode Island, Department of Environmental Management. The encouragement and interest of D. Sanning and S. James of the EPA are especially noted. Subcontracted field services not mentioned in the text were provided as follows: test borings and well installation by R. F. Geisser and Associates, Inc. and Guild Drilling Co., Inc.; laboratory services by Energy Resources Company (ERCo); topographic surveying by Caputo and Wick, Ltd.; and geotechnical support by Geotechnical Engineers, Inc.

The contributions to the site investigation of Paul J. Stoller of MITRE are also acknowledged. The results and conclusions presented are those of the authors and do not necessarily reflect the views of the sponsoring agencies or other subcontractors.

Portions of this paper were presented at the EPA National Conference on the Management of Uncontrolled Hazardous Waste Sites, October 15-17, 1980, Washington, D.C. and appear in the proceedings under the title: "Remote Sensing for Investigating Buried Drums and Subsurface Contamination at Coventry, Rhode Island" by H. J. Yaffe, N. L. Cichowicz, and P. J. Stoller.

REFERENCES

1. Cichowicz, N.L., R.W. Pease, P.J. Stoller, and H.J. Yaffe. 1980. Evaluation of Abatement Alternatives: Picillo Property, Coventry, Rhode Island. MITRE Technical Report-80W 00253, The MITRE Corporation, Bedford, Massachusetts. 83pp.
2. Cichowicz, N.L., R.W. Pease, P.J. Stoller, and H.J. Yaffe. 1980. Use of Remote Sensing Techniques in a Systematic Investigation of an Uncontrolled Hazardous Waste Site. MITRE Technical Report-80W00244, The MITRE Corporation, Bedford, Massachusetts. 69pp.
3. Pease, R.W. et al. 1980. Hazardous Waste Investigation: Picillo Property, Coventry, Rhode Island. MITRE Technical Report-80W00032, The MITRE Corporation, Bedford, Massachusetts. 142pp.

CONCEPTUAL COST ANALYSIS OF REMEDIAL ACTIONS AT UNCONTROLLED SITES

HOWARD L. RISHEL
SHEILA M. KENNEDY
SCS Engineers
Long Beach, California 90802

OSCAR W. ALBRECHT
U.S. Environmental Protection Agency
Municipal Environmental Research Laboratory
Cincinnati, Ohio 45268

ABSTRACT

A document has been prepared, in response to the 1980 "Superfund" legislation, which gives enforcement officials a tool with which they can quickly compare the relative costs of several remedial action scenarios at inactive landfill and surface impoundment disposal sites. This report outlines the process of costing remedial action unit operations (at a range of site sizes), and combining the unit operations to yield relative cost data for an entire remedial action scenario. Examples are given of costing one unit operation at five scales of portrayal, and of costing one remedial action scenario which is comprised of several unit operations. The assumptions and limitations of the methodology are given.

Introduction

During 1980, the U.S. Congress enacted "Superfund" legislation, which was proposed to provide funds for the U.S. Environmental Protection Agency (EPA) to assist in the mitigation of pollution problems at uncontrolled waste disposal sites through remedial actions. The responsible offices within EPA (the Oil and Special Materials Division, and the Office of Enforcement) requested the Office of Research and Development to provide technical information to support this process. As a part of this effort, SCS Engineers undertook to review, compile, update, and integrate existing data on the costs of such remedial actions, in terms of discrete unit operations which could then be combined to construct conceptual remedial action scenarios.

This type of review-and-update approach was considered more appropriate than additional conceptual designs efforts because much conceptual design work has already been done. The design work which exists, however, is scattered, incomplete, and inconsistent in methodology; much of it is out of date, and vague either about the methods used to arrive at a cost figure or about what components the cost figure included.

Through the review-and-update approach, we hope to impose a consistent methodology on the existing data in terms of scope, location, time frame, and cost computations. In addition, we hope to flesh out the missing details, where necessary, and present the

TABLE 1. SCALES OF OPERATION FOR LANDFILL DISPOSAL SITES

Scale of Operation	Refuse-to-Soil Ratio
1. 9.07 tonnes/day	1:1
2. 45.36 tonnes/day	1.5:1
3. 90.72 tonnes/day	2:1
4. 272.16 tonnes/day	3:1
5. 453.60 tonnes/day	4:1

results in a uniform format, with a minimum of overlap between the individual unit operations. The resulting document presents this existing data in a framework of a broad and consistent methodology, with enhanced detail.

It should be emphasized here that no new conceptual design work was done for this project. Where data was incomplete, some detail was filled out, but the thrust of this work was to enhance previously existing conceptual design data and make them more available and useful to enforcement personnel responsible for overseeing the retrofit operations.

Because the document was intended for use in the retrofitting of uncontrolled sites, the unit operations examined are limited to those appropriate for the clean-up of closed or abandoned sites.

Methodology

In developing and characterizing unit operations for remedial action at waste disposal sites, we developed hypothetical site profiles and their associated unit operation profiles. Costs for each unit operation at five scales of site operation were then computed at three cost levels: high and low U.S. averages, and the price estimate for a single city, Newark, NJ (mid-1980 dollars).

Site Profiles

Site profiles, or hypothetical disposal sites, were developed for landfill disposal and for surface impoundments (disposal ponds). Each of these was portrayed at five scales of daily operation. The resulting site profiles were configured to conform to uniform sets of design criteria and environmental conditions. For both landfills and surface impoundments, the selected scales of operation were developed in terms of daily input. This emphasis on daily input is consistent with the usual view of landfill practices and the assumptions that surface impoundments are intended as temporary storage, with relatively short retention times.

Landfills--Table 1 shows the scales of operation for landfill disposal sites. The range of scale sizes was developed from data presented in References (2) and (7).

Although the scale of operation for each landfill is different, the following design criteria are held constant:

- The surface area for each landfill is square.
- All landfills are cut and cover operations, with cut slopes at a 2:1 ratio and fill slopes at a 3:1 ratio.

TABLE 2. SCALES OF OPERATION FOR SURFACE IMPOUNDMENTS

Scale of Operation (Influent)	Detention Time
1. 10 m^3/day	3 days
2. 50 m^3/day	3 days
3. 500 m^3/day	10 days
4. 5,000 m^3/day	10 days
5. 50,000 m^3/day	10 days

- Operation at each landfill was 260 days/year for ten years before the site was closed.

- The compaction rate was 0.596 tonnes/ compacted m^3.

Figures 1 and 2 show the layout of the hypothetical landfill site, without reference to the scale of operation.

To allow comparison of remedial actions between sites operating at different scales, the following environmental conditions are also held constant:

- Ground surface and ground water gradient are at a 1% slope.

- Ground water is 4.0 m (13.1 ft) below the ground surface.

- Low permeability strata ($<10^{-6}$ cm/ sec) is 15 m (50 ft) from the ground surface.

- Unconsolidated earth materials have a permeability of 10^{-5} cm/ sec or greater.

Surface Impoundments--Table 2 shows the scales of operation for surface impoundments. The range of scale sizes was developed from data in References (3) and (8). In this case, the scale of operation is given in terms of cubic meters of influent.

Figure 3 shows the plan of the hypothetical surface impoundment without reference to the scale of operation. The following design criteria were common to all of the surface impoundment site profiles:

- The ponds are square and unlined.

- Berms were constructed from soils excavated during pond construction, and have 3:1 side slopes.

- The site operated 365 days/ year for ten years before closure or abandonment.

- Sediment was removed from pond bottom every two years.

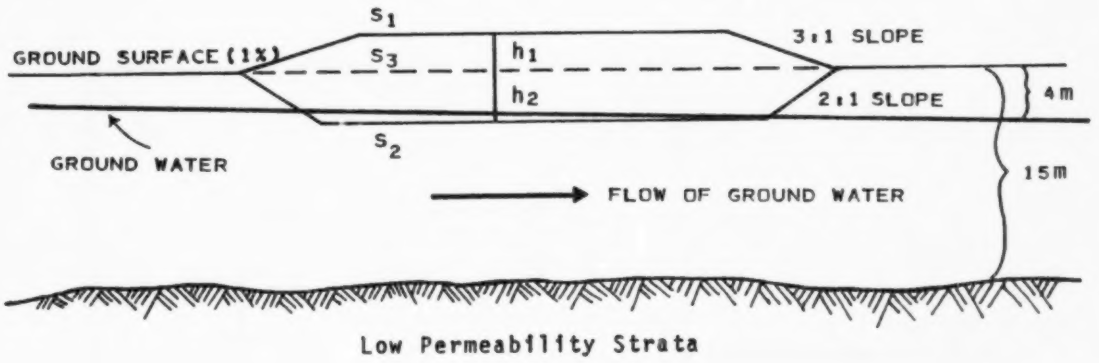
- Wastewater contained 100 mg/l settleable solids.

- Density of solids was 2 g/ml.

- Sludge is 70% moisture by weight when removed.

- Wastewater was recirculated after allowing 3 to 10 days for solids settling.

- Because of short detention time and sludge on bottom, precipitation, evaporation,


S1
S3
h1
h2
S2
GROUND SURFACE (1%)
GROUND WATER
3:1 SLOPE
2:1 SLOPE
4 m
15 m
FLOW OF GROUND WATER
Low Permeability Strata

Where:

T_L = Total volume of refuse (m^3)
D_L = Total volume of soil (m^3)
h_1 = Height of landfill above ground surface (m)
h_2 = Depth of landfill below ground surface (m)
S_1 = Top side of landfill (m)
S_2 = Bottom side of landfill (m)
S_3 = Side of landfill at ground surface (m)
A = Area of landfill at ground surface (m^2)

Figure 1. Typical side view of landfill.

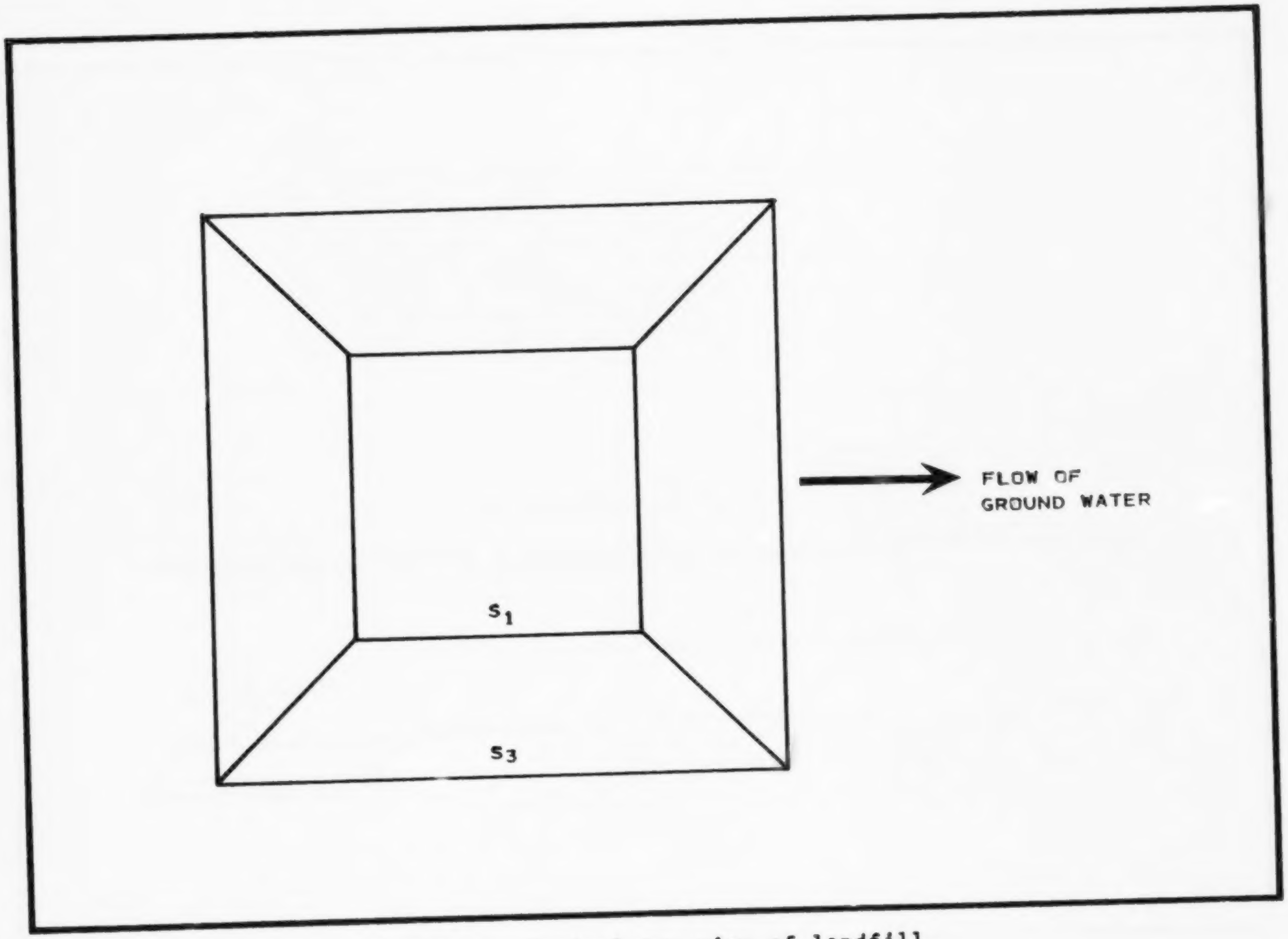
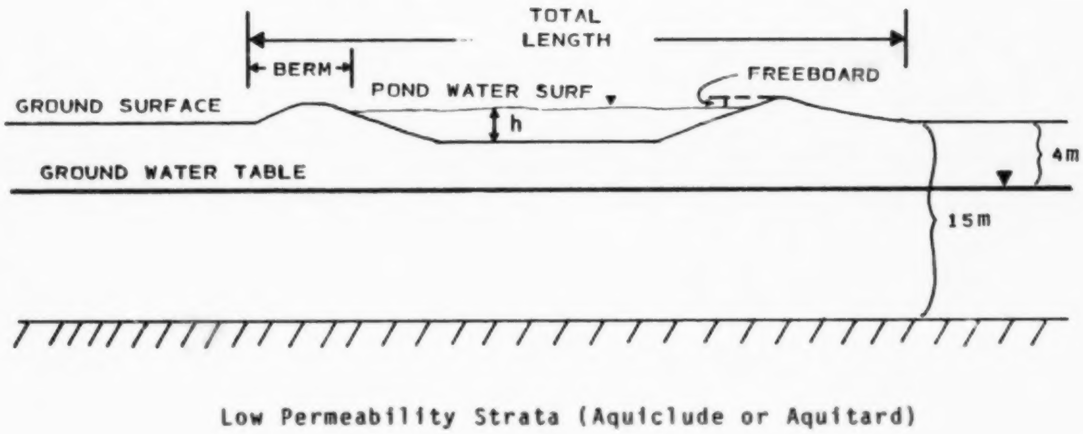

FLOW OF
GROUND WATER
S_1
S_3

Figure 2. Typical top view of landfill.


TOTAL LENGTH
BERM
FREEBOARD
POND WATER SURF
GROUND SURFACE
h
4m
GROUND WATER TABLE
15m
Low Permeability Strata (Aquiclude or Aquitard)

Where:

- (Total length)^2 = impoundment surface area.
- Berm side slopes constructed at 3 horizontal to 1 vertical.
- Berm top width nominal 2m, maximum 3 meters.
- 0.5m freeboard designed into all ponds.

Figure 3 . Side view of surface impoundment and percolation losses are considered negligible when compared to the volumes involved.

- Average percolation ≤ 8.14 l/day/m^2 (0.2 gal/day/ft^2).

To help compare remedial actions for each of the scales of operation, the following environmental conditions surrounding each pond were developed:

- Ground surface and ground water gradient are at a 1% slope.
- Ground water is 4.0 m (13.1 ft) below the ground surface.
- Low permeability strata (aquiclude or aquitard; $K<10^{-6}$ cm/sec) located at 15 m (50 ft) from ground surface.
- Unconsolidated earth materials have a permeability of $\geq 10^{-5}$ cm/sec.

Unit Operation Profiles

Thirty-five unit operations were identified which might be used as part of a remedial action effort at an uncontrolled hazardous waste disposal site. These operations are shown in Table 3 for both impoundments and landfills. Examination of this table shows some apparent overlap between the two lists, but in fact each operation was configured separately for the distinctly different design criteria and environmental conditions assumed in each site profile.

All of the unit operations shown were drawn from the literature and only those for which the literature contained adequate conceptual designs and cost data were addressed. In some cases a part of the necessary data was missing and was supplied by us.

Alternative unit operations--When a pollution problem exists, a number of unit operations may be used interchangeably. The following list gives some unit operations which may be used either conjunctively or as alternatives for each other.

1. For elimination of contaminated site runoff, and prevention of precipitation from entering a landfill or closed impoundment, the following are conjunctive or alternative unit operations:
   - Contour grading and surface water diversion
   - Surface sealing
   - Revegetation
   - Berm construction/reconstruction.
2. For prevention of leachate formation, the following are conjunctive/alternative unit operations:
   - Contour grading and surface water diversion
   - Surface sealing
   - Grout curtain
   - Sheet piling
   - Slurry trench
   - Well extraction
   - Well point system
   - Chemical fixation.
3. For the control of leachate/contaminated ground water migration, the following are conjunctive/alternative unit operations:
   - Grout curtain
   - Grout bottom seal
   - Sheet piling
   - Slurry trench
   - Well point system
   - Well extraction
   - Well injection
   - Underdrains.
4. For gas (methane and other volatile hydrocarbons), the following are conjunctive/alterna-tive unit operations:
   - Perimeter gravel trench
   - Gas migration control - passive

TABLE 3. UNIT OPERATIONS USED AS REMEDIAL ACTIONS

Landfills

1. Contour grading and surface water diversion
2. Surface sealing
3. Revegetation
4. Bentonite slurry trench cutoff wall
5. Grout curtain
6. Sheet piling cutoff wall
7. Bottom sealing
8. Drains
9. Well point system
10. Deep well system
11. Injection
12. Leachate handling by subgrade irrigation
13. Chemical fixation
14. Chemical injection
15. Excavation and reburial
16. Ponding
17. Dike construction
18. Perimeter gravel trench
19. Treatment of contaminated waste
20. Gas migration control - passive
21. Gas migration control - active

Impoundments

22. Pond closure and contour grading of surface
23. Surface sealing of closed impoundment
24. Revegetation
25. Slurry trench cutoff wall
26. Grout curtain
27. Sheet piling cutoff wall
28. Grout bottom seal
29. Toe and underdrains
30. Well point system
31. Well extraction system
32. Well injection system
33. Leachate treatment
34. Berm reconstruction
35. Excavation and disposal at secure landfill

- Gas migration control - active.

Cost Compilation

Once a remedial action unit operation was defined in terms of its intended use (with respect to the landfill or surface impoundment site profiles) and the extent to which it could be used in conjunction with or as an alternative to other unit operations, the cost of the operation was defined for each scale of operation associated with the site profiles. To do this, the unit operation was broken down into component requirements. Each component was further defined in terms of sub-components (labor, materials, and equipment), and costs were assigned to each component and subcomponent. The assigned costs are in terms of mid-1980 dollars for U.S. upper and lower cost averages (for the continental 48 states), as well as for the example location of Newark, NJ.

After costs were assigned to each component, conceptual design capital and operating cost estimates were accumulated and allowances for overhead and contingencies were applied. Total and average life cycle costs were then computed for each scale of unit operation. These cost averages were then plotted and graphically interpolated to estimate scale economies for each unit operation.

Estimation of Component Costs- For the most part, the 1980 Dodge and Means Guides (4,6) were used to obtain the costs needed. The costs were then expressed in terms of metric units.

Regional adjustment indexes presented in the Dodge Guide (4) were used to modify the metric versions of the cost estimates for geographical differences. These indexes were applied to obtain revised material and labor costs for the U.S. low, U.S. high, and Newark, NJ estimates. No index was applied to equipment costs, since it was assumed that equipment costs are the same nationwide. Because the Dodge Guide (4) and Means (6) present costs differently, assumptions were made so that the regional adjustment indexes could be used for both texts. For example, in the Means, labor costs were not identified as a separate entry, but were included as part of installation. Thus, whenever the Means was used to present costs, the Dodge Guide Regional Adjustment Index for Labor was applied to installation costs.

Frequently, both Dodge and Means did not itemize costs into categories of labor, material, and equipment, but simply presented a "total" estimate. Depending upon which reference was used, the following rules were applied: in the Dodge Guide, if only a total cost was presented, an average labor/material index was applied to the unit cost; in the Means, the "total" costs include an overhead allowance of 25%. This allowance was removed before the labor/material index was applied. In all cases, costs were adjusted so that overhead allowances were not included at the subcomponent level.

As the scale of operation changed, the quantity of any one component required for a unit operation also changed. The cost of each component presented in the unit operation conceptual design cost tables typically includes the sum of costs for any material, labor, or equipment subcomponents. These total costs for each component do not include overhead and contingencies. Once all the components within a unit operation were costed, the costs were summed, giving a subtotal capital cost for the unit operation. This subtotal capital cost was then used to obtain an overhead allowance (always 25%), and a contingency allowance (between 10 and 40%, depending upon the unit operation). The subtotal capital cost was added to the overhead and contingency allowances to obtain the estimate of total unit operation capital cost. (See example below.) This method was

TABLE 4. DERIVATION OF INFLATION RATES FOR O&M INPUTS

Type of O&M Input	Electricity	All Other O&M Inputs
Related Published Cost Index:	Electric Power	Consumer Price (CPI-W)
March 1980 Index Value:	305.7	239.9
Average Annual Index Percent Increase Since Base Year (i.e., 12.75 years since mid-1967 when index equaled 100):	9.160%	7.104%
Assumed Future Inflation Rate:	9.2%	7.1%

used for all scales of unit operation.

Life Cycle Costing--Once total capital and operating costs were determined for lower and upper U.S. averages and for Newark, total and average life cycle costs were computed to en-ure that any subsequent cost comparisons of unit operations could be equitably accomplished.

Although operation and maintenance (O&M) cost estimates are for 1980, as the first year of operation, O&M component quantity requirements were estimated to accurately reflect requirements for each of the first ten years of remedial operations. This 10-year life of the conceptual designs means that life cycle evaluation of operating costs only addressed subsequent inflation and appropriate discounting of these O&M components costs to their mid-1980 present values. It was further assumed that capital costs would not be amortized and discounted, but would be considered as fully incurred in the first year of operation. As a result of these assumptions, average annual compounding inflation rates for electricity and for all other O&M components were derived using estimates from the April 1980 Survey of Current Business (1). These inflation rates were derived as shown in Table 4.

In determining the present values of future expenditures, the March 1980 Gross National Product Implicit Price Deflator of 174.51 (5) was similarly evaluated in terms of its 1972 base year to estimate an annual general inflation rate of 7.4%. To this, an assumed 4% social time preference rate was added to create a total annual discount rate of 11.4%. The life cycle cost methodology was then followed, in which inflated operating costs were discounted to their mid-1980 present values, and summed with total capital costs, to determine total life cycle costs over the 10-year life span of each unit operation. Average life cycle costs were then computed by dividing this total by the site profile's daily scale of operation.

The contract report of this work includes a set of tables for each unit operation, giving the cost of each component, plus overhead and contingency allowances, O&M costs, and life cycle costs, at each scale of operation. One set of these tables is given as part of the costing example below (Tables 5-10).

Scale Economies--The averages found by dividing total life cycle costs by the daily acceptance rates of the site profiles were plotted and graphically interpolated to determine unit operation scale economies. Graphical interpolation by visually fitting curves to the points was performed in preference to statistical curvefit techniques.

It should be emphasized that although the upper and lower curves represent the "typical" range in life cycle average costs, they were derived using Dodge Guide city index numbers for labor and material subcomponents. As a result, they do not represent extremes, and are not statistically derived confidence bounds.

These figures (one for each unit operation) are given in the contract report of this work, and an example is given below (Figure 4).

Example unit operation

An example of remedial action unit operation can be taken in the revegetation of a landfill (Unit Operation 3, Table 3). All other unit operation were derived similarly and reported in the same format in the contract report; each consisted of six tables, followed by one figure.

Table 5 describes this unit operation in general terms, beginning with a brief statement regarding the use of this unit operation. It then provides a description of how this operation is configured, and which other unit operations are commonly used in conjunction with revegetation. The table ends with the critical assumptions for applying this unit operation to the site profiles. This format is followed in each of the general description tables.

The next five tables describe how the revegatation unit operation would be achieved for each of the five scales of landfill operation. Table 6 shows the component requirements and their associated costs when the revegetation unit operation is applied to the 9.07 tonnes/day landfill site. In this table both capital and O&M component requirements are identified and costed in terms of mid-1980 dollars.

As mentioned previously, the costs associated with each component may represent the sum of various labor, material, and equipment costs incurred in accomplishing that component. For example, costs for the "mulching" component are for applying mulched hay over 9.86 ha (2.43 acres). The labor costs, according to the 1980 Dodge Guide, are typically $14.00/ha ($34.50/acre). This number was adjusted for regional labor cost differentials and multiplied by the number of hectares involved; these labor costs ranged from $50 to $110. The value for Newark, NJ was $100. Material (hay) and equipment costs were added to these labor costs to obtain the mulching cost estimates seen in Table 6. A similar process was followed in costing each capital and O&M component.

Once all of the capital components had been identified and costed, allowances for overhead and contingencies were added to complete the capital cost portions of these estimates. In all unit operations a 25% overhead allowance was assumed. This assumption is partly based on the fact that the Means construction cost guide (6) also assumes a 25% allowance for contractor's overhead. A contingency allowance to cover unforseen cost additions was also applied to each captial cost subtotal. In general, the contingency allowance ranged from 10% to 40% depending on the extent to which the unit operation was expected to encounter unforseen difficulties.

As explained previously, each of the O&M component costs were escalated for future inflation and then discounted to their present values (in mid-1980 dollars). These present values were summed

TABLE 5. UNIT OPERATION 3 - REVEGETATION

Use: Revegetation helps to physically stabilize the earth material and reduce infiltration; it also serves to minimize erosion of the cover material by wind and water.

Configuration: Revegetation involves first grading the landfill, covering it with a suitable, fertile soil, adding soil supplements, and then seeding.

Conjunctive Uses: Contour grading and gas migration control systems are used as cost components.

Assume:
a) Entire surface of landfill is revegetated.

b) 0.6m of clay and silt loam will be used for landfill cover.

c) Clay and silt loam are easily accessible; transportation costs are not included.

d) Mulch will be used to stabilize soil until vegetation takes hold.

e) Native grasses will be used for seed.

TABLE 6. REVEGETATION UNIT OPERATION AT LANDFILL OPERATION OF 9.07 TONNES/DAY

	Total Unit $		
Capital Cost of Components (mid-1980)	Lower U.S.	Upper U.S.	Newark, NJ
Area Preparation	670	1,160	1,040
1) Excavation and Grading Refuse (5,130 m^3)	8,130	9,420	9,090
2) Hydroseeding	880	1,240	1,110
3) Soil Supplements			
4) Mulching	270	390	350
Capital Cost (subtotal)	9,950	12,210	11,590
Overhead Allowance (25%)	2,490	3,050	2,900
Contingency Allowance (10%)	1,000	1,220	1,160
Capital Cost Total	13,440	16,480	15,650
O & M Costs			
a) Grass Mowing (2.43 acres) (6 mowings/year)	420	660	600
Refertilization (2.43 acres) (1 x per year)	240	390	340
O & M Cost Total	660	1,050	940
Total Life* Cycle Cost (over 10 years)	19,000	25,330	23,570
Average Life* Cycle Cost (By tonnes/day)	2,090	2,790	2,600

*See Text for Methodology and Assumptions.

TABLE 7. REVEGETATION UNIT OPERATION AT LANDFILL OPERATION OF 45.36 TONNES/DAY

Capital Cost of Components (mid-1980)	Total Unit $ Lower U.S.	 Upper U.S.	 Newark, NJ
Area Preparation	2,290	3,960	3,540
1) Excavation and Grading Refuse (17,075 m^3)	27,030	31,330	30,250
2) Hydroseeding 3) Soil Supplements	2,990	4,220	3,780
4) Mulching	910	1,300	1,170
Capital Cost (subtotal)	33,220	40,810	38,740
Overhead Allowance (25)	8,300	10,200	9,690
Contingency Allowance (10%)	3,320	4,080	3,870
Capital Cost Total	44,840	55,090	52,300
O & M Costs			
a) Grass Mowing (8.23 acres) (6 mowings/year)	1,320	2,220	1,980
Refertilization (8.23 acres) (1 x /year)	820	1,320	1,150
O & M Cost Total	2,140	3,540	3,130
Total Life* Cycle Cost (over 10 years)	62,880	84,930	78,690
Average Life* Cycle Cost (By tonnes/day)	1,390	1,870	1,730

*See Text for Methodology and Assumptions.

TABLE 8. REVEGETATION UNIT OPERATION AT LANDFILL OPERATION OF 90.72 TONNES/DAY

Capital Cost of Components (mid-1980)	Total Unit $ Lower U.S.	 Upper U.S.	 Newark, NJ
Area Preparation	3,710	6,440	5,760
1) Excavation and Grading Refuse (27,685 m^3)	43,820	50,790	49,050
2) Hydroseeding 3) Soil Supplements	4,860	6,860	6,130
4) Mulching	1,480	2,120	1,910
Capital Cost (subtotal)	53,870	66,210	62,850
Overhead Allowance (25)	13,470	16,550	15,710
Contingency Allowance (10%)	5,390	6,620	6,290
Capital Cost Total	72,730	89,380	84,850
O & M Costs			
a) Grass Mowing (13.38 acres) (6 mowings/year)	2,160	3,600	3,240
Refertilization (13.38 acres) (1 x 1 year)	1,340	2,140	1,870
O & M Cost Total	3,500	5,740	5,110
Total Life* Cycle Cost (over 10 years)	102,240	137,770	127,930
Average Life* Cycle Cost (By tonnes/day)	1,130	1,520	1,410

*See Text for Methodology and Assumptions.

TABLE 9. REVEGETATION UNIT OPERATION AT LANDFILL OPERATION OF 272.12 TONNES/DAY

	Total Unit $		
Capital Cost of Components (mid-1980)	Lower U.S.	Upper U.S.	Newark, NJ
Area Preparation	8,770	15,230	13,610
1) Excavation and Grading Refuse (65,100 m^3)	103,060	119,440	115,350
2) Hydroseeding	11,490	16,220	14,510
3) Soil Supplements			
4) Mulching	3,490	5,010	4,500
Capital Cost (subtotal)	126,810	155,900	147,970
Overhead Allowance (25)	31,700	38,980	37,000
Contingency Allowance (10%)	12,680	15,590	14,800
Capital Cost Total	171,190	210,470	199,770
O & M Costs			
a) Grass Mowing (31.65 acres) (6 mowings/year)	5,100	8,520	7,620
Refertilization (31.65 acres) (1 x/year)	3,170	5,060	4,430
O & M Cost Total	8,270	13,580	12,050
Total Life* Cycle Cost (over 10 years)	240,910	324,950	301,350
Average Life* Cycle Cost (By tonnes/day)	890	1,190	1,110

*See Text for Methodology and Assumptions.

TABLE 10. REVEGETATION UNIT OPERATION AT LANDFILL OPERATION OF 453.60 TONNES/DAY

	Total Unit $		
Capital Cost of Components (mid-1980)	Lower U.S.	Upper U.S.	Newark, NJ
Area Preparation	12,680	22,020	19,680
1) Excavation and Grading Refuse (93,935 m^3)	148,710	172,340	166,430
2) Hydroseeding 3) Soil Supplements	16,600	23,460	20,970
4) Mulching	5,060	7,250	6,510
Capital Cost (subtotal)	183,050	225,070	213,590
Overhead Allowance (25%)	45,760	56,270	53,400
Contingency Allowance (10%)	18,300	22,510	21,360
Capital Cost Total	247,110	303,850	288,350
O & M Costs			
a) Grass Mowing (45.74 acres) (6 mowings/year)	7,380	12,360	10,980
Refertilization (45.74 acres) (1 x/year)	4,570	7,320	6,400
O & M Cost Total	11,950	19,680	17,380
Total Life* Cycle Cost (over 10 years)	347,850	469,760	434,870
Average Life* Cycle Cost (By tonnes/day)	770	1,040	960

*See Text for Methodology and Assumptions.

over a 10-year life cycle of future site maintenance and then added to the capital cost total to determine total life cycle cost. Average life cycle cost was computed by dividing this total by the landfill's former daily scale of operation.

Similar cost analyses for applying revegetation to the other scales of landfill operation appear in Tables 7-10.

The life cycle average costs from Tables 6-10 were plotted in Figure 4. As mentioned above, the cost points on Figure 4 are average life cycle costs per tonne of waste deposited during the daily operation of the landfill. The curves presented on this figure were created by visually interpolating between the points to graphically depict scale economies. Because of the small number of points per curve, statistical curvefit methods were not attempted.

Application and limitations

The contract report document produced as a result of this review-and-update work consists primarily of unit operation costs at the component and sub-component levels, and average life cycle costs for each scale of operations. By applying this cost information to the report's discussion of alternative or conjunctive unit operations, enforcement personnel will be able to configure and cost complete remedial action scenarios.

The following is an example of how a remedial action scenario involving several unit operations may be costed by using the scale economy figures for each constituent unit operation. The scale of operation was purposely selected to be different from the scales used in developing the unit operation conceptual design cost estimates.

The Problem

The hypothetical hazardous waste landfill site is producing leachate from surface water intrusion; the leachate is contaminating nearby ground water. It has also been found that the bottom 1 m of the landfill is in ground water. The scale of operation is 300 tonnes/day.

Remedial Action Scenario Solution

The solution presented here is only one of many ways that the problem outlined above may be reduced, and is given to show how a long-term response action can be developed for a problem site. The solution uses the following unit operations as part of the remedial action scenario:

- Contour grading and surface water diversion.
- Revegetation.
- Sheet piling cutoff wall.

Contour grading and surface water diversion promote and channel surface water runoff by grading the landfill and creating earth berms to drain water away from the landfill. Revegetation helps to stabilize the earth materials and reduce infiltration. The sheet piling cutoff wall is used as a physical barrier to lower the water table around the landfill, so that the waste present is no long saturated.

Table 11 is a breakdown of average life cycle costs for unit operations used to clean up a landfill which received 300 tonnes/day of hazardous waste during its operational days. Each of the figures shown was obtained by reading the average life cycle cost curve for that unit operation at the stated scale of operation. The unit operation costs are then summed to give the total average life cycle cost for the proposed remedial action scenario.

It should be pointed out that although this process of reading costs from figures is not necessarily inappropriate for certain

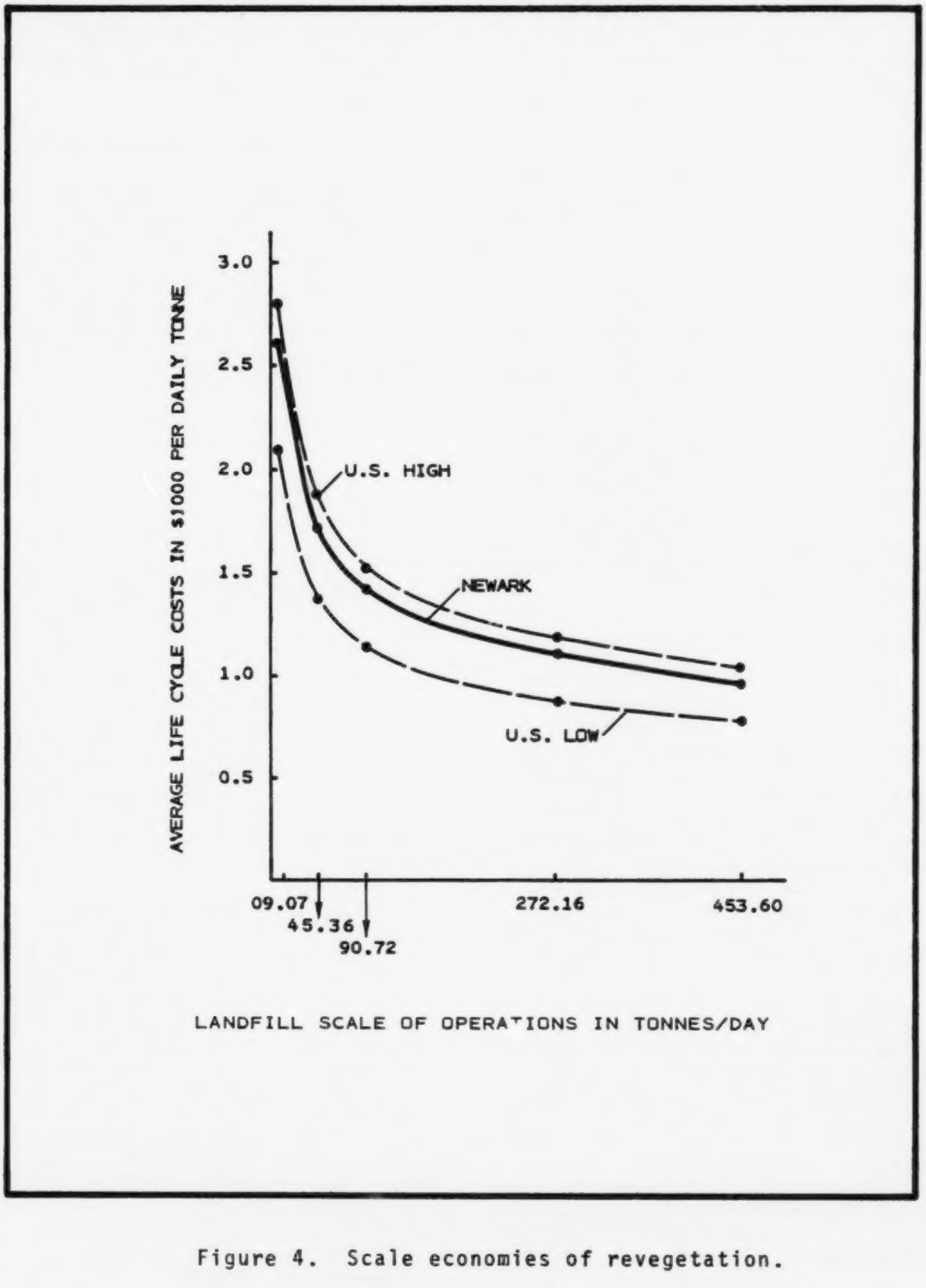


Figure 4. Scale economies of revegetation.

TABLE 11. LONG-TERM REMEDIAL ACTION AVERAGE LIFE CYCLE COSTS FOR A 300-TONNE/DAY LANDFILL

Unit Operations	Lower U.S.	Upper U.S.	Newark, NJ
Contour Grading and Surface Water Diversion	730	870	840
Revegetation	850	1,180	1,080
Sheet Piling Cut-off Wall	4,500	6,500	5,600**
Total Average Life Cycle Costs	6,080	8,550	7,520

applications, it does introduce measurement errors. It may also ignore component duplications or scale economies resulting from the combination of several related unit operations.

While the intention of this unit operation costing is to allow comparison of the relative costs of several remedial action scenarios, it must be emphasized that the resulting cost figures are averages and not absolute costs. The U.S. high and low figures do not represent actual limiting values, but give an average of ranges across cities in the continental United States. Because these figures are averages and not absolutes, they should not be used to determine the actual or expected cost of a remedial action scenario, but to compare the relative costs of several scenarios.

Factors which should be considered by anyone using the document are: 1) the costs for equipment are not permitted to vary across the nation, and 2) all costs are in terms of mid-1980 dollars, except O&M costs.

Summary

A total of thirty-five conceptual design unit operations, addressing either landfill or surface impoundment disposal sites, were identified in the literature and their cost estimates were updated. The results were presented in terms of a consistent format and methodology.

As part of this updating process, revised site profiles for landfill and impoundment conditions were developed at each of five scales of operation. Remedial action unit operation conceptual designs appearing in the literature were then refined to best address each operating level of these landfill or impoundment site profiles.

Costs were estimated for each of the unit operations according to a consistent computational methodology, in which capital and operating cost estimates were combined to determine total and average life cycle costs for the example location of Newark, NJ, as well as for the average lower and upper U.S. costs, within the continental states. All costs were estimated in terms of mid-1980 dollars.

The average life cycle costs for each unit operation were plotted against the five scales of site operation. Cost curves were graphically interpolated between point estimates to determine unit operation scale economies.

Because complete remedial action scenarios for uncontrolled sites typically consist of several unit operations, much remains to be done, even from a conceptual design cost perspective, in identifying and costing the most promising scenarios. Such an effort might include a systematic evaluation to determine the most prevalent pollution problems occurring at uncontrolled landfill and impoundment sites. Once this set of "typical" pollution cases has been determined, likely remedial action scenarios could be configured using unit operations developed in this study. The resulting composite cost estimates for these scenarios could then be compared to determine the relative cost advantages of each alternative.

References

1. Current Business Statistics. Survey of Current Business, Vol. 60, No. 4 U.S. Department of Commerce, Bureau of Economic Analysis. April 1980.

2. Fred C. Hart Associates, Inc. Analysis of the Technology, Prevalence and Economics of Landfill Disposal of Solid Waste in the United States - Volume II. EPA Contract No. 68-01-4895, U.S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C. 1979. 97 pp.

3. Geraghty and Miller, Inc. Surface Impoundments and Their Effects on Ground-Water Quality in the United States. EPA-570/9-78-004, U.S. Environmental Protection Agency, Office of Drinking Water, Washington, D.C. 1978. 275 pp.

4. McMahon, L. A. 1980 Dodge Guide to Public Works and Heavy Construction Costs. McGraw-Hill, New York, New York. 1979.

5. National Income and Product Tables. Survey of Current Business, Vol. 60, No. 4. U.S. Department of Commerce, Bureau of Economic Analysis. April 1980.

6. Robert S. Means Company, Inc. Building Construction Cost Data 1980. 1979. 371 pp.

7. SCS Engineers. Study of Ongoing and Completed Remedial Action Projects: Survey Results and Recommended Case Studies. Environmental Protection Agency Solid and Hazardous Waste Research Division, Cincinnati, Ohio. 1980.

8. SCS Engineers. Surface Impoundment Assessment in California. EPA Contract No. 68-01-5137, U.S. Environmental Protection Agency, Office of Drinking Water, Washington, D.C. 1980.

REGULATING ILLEGAL DUMPING OF HAZARDOUS WASTES

Edward Yang, Bob Anderson, and Roger Dower
Environmental Law Institute
Washington, D.C. 20036

ABSTRACT

Efficient regulation of hazardous waste management practices is an important conerstone of implementation of Resource Conservation and Recovery Act (RCRA). However, efficient regulations can not be achieved without considering compliance as an important variable in determining appropriate level of standards and requirements of the regulations. In order to do this, our paper develops a compliance model based on the relative costs of compliance and noncompliance. The model assumes the financial consideration of the hazardous waste managers to be the primary motivation to comply or not. The model is constructed on an industry level to address the policy-makers' concern on the percentage of industry compliance. The model also allows the policy-makers to weight the analysis by the various policy variables, such as number of firms, employment size, value of shipment and enforcement strategy. Using the data gathered from several case studies of illegal dumping of hazardous waste, the model was partially applied to show the cost differential between proper and improper management practice. Although the data limitation prevented a full operation of the model, the possible effects of compliance cost on the level of industry compliance are demonstrated.

Introduction

In the past, environmental management models have often stressed deriving a socially optimal level of regulation where social demand for environmental quality equals the social supply of it.[1] The application of the models has encountered several difficulties. First, the determination of an optimal level of environmental quality, is often done in the political arena which is difficult to be explicitly incorporated into the model, since it is based on a social preference function. Second, even for a given set of social preferences, the difficulty of measuring social welfare loss due to misallocation of resources often deters the operation of the model, Third, much of the regulatory inefficiency may come from not using the environmental standard in a most efficient way, rather than from not being able to determine the socially optimal level of environmental quality. The first two difficulties have been recognized and dealt with by a large body of social and economic research.[2] However, it is only recently that the inefficiency involved in standard or criteria setting has been rigorously examined.[3] This paper examines the problem of illegal dumping of hazardous waste in the light of such inefficiency through the use of a compliance model.[4,5] The use of a compliance model is especially important for regulations that are difficult to enforce, such as illegal dumping of hazardous waste, where the release of waste is often undetected and its harmful effects are difficult to demonstrate.

Until recently the implicit assumptions underlying environmental regulatory analyses have often been that the question of compliance is a separate issue from the one of determining optimal level of environmental protection. When such assumption is unrealistic, the net effect is that the social cost of regulation becomes underestimated. In these analyses where the optimal level of pollution abatement is determined by the demand and supply of the abatement, such underestimation can provide misleading results. In reality, full compliance can not be taken for granted. Furthermore, the setting of regulatory requirement inherently influences the level of compliance through compliance cost. In other words, the cost of compliance becomes a crucial variable in determining the success of the regulatory mechanism.

In studying hazardous waste policy we are interested in the relationship between the cost of complying with the RCRA regulations and cost incurred by illegal dumping. Prior to RCRA, much of the improper release or dumping of the waste was done to save disposal cost. Although, some careless dumping may have arisen from ignorance concerning the hazardous nature to the waste, to perceive all of the past improper waste disposal activities as being caused by ignorance is naive. Costs do affect a Firm's decisions; even with strict RCRA regulations defining hazardous wastes and their legal disposal, improper disposal will continue as long as there is a significant reduction in disposal costs resulting from noncompliance.

On the applied level, the purpose of this paper is to examine the effects of RCRA on illegal dumping. More specifically, we can ask the question, "Will RCRA regulations promote the optimal amount of compliance?" The very posing of this question implies that we are not taking full industry compliance for granted. Furthermore, the question implies that the level of compliance may depend on the stringency and structure of the regulations. We will direct our attention to the financial factors underlying the decision to comply. The groundwork for our compliance model appeared in the literature on the economics of crime.6 However, it was not until Viscusi and Zeckhauser's recent work on optimal standards that the level of compliance was linked to the cost of compliance. Their work showed that there is a point in setting standard beyond which further tightening of that standard will reduce the overall effectiveness of the regulation. The regulator should strive to approach that point as closely as possible without going beyond it. Although, the work is pathbreaking in its theoretical content, the application of this model remains to be attempt; the information requirement of this model is prohibitive.

In pursuing the purpose of this paper, we have put some effort into reconstructing the Viscuci and Zeckhauser (VZ) model so that it can be more susceptible to application. We will first illustrate the concept of optimal standard through a number of graphs and then proceed to construct a model that can utilize information on cost differential between compliance and noncompliance. The model will also allow the regulator to perceive compliance from an industry level, given information on the cost differential distribution across the industry. In addition, the policy maker will be able to weigh the criteria for choosing optimal standard with policy variables of his or her concern. The advantage of this model is that it can be utilized on several levels depending upon the availability of relevant information. We will show that in the case of full information the optimal standard can be easily derived.

Ideally, the paper would then proceed to apply the above model to determine whether the RCRA regulatory requirements are optimal in soliciting the maximum level of industry compliance. But even on the simplest level of the above model such a task is beyond the resources of this study; considerable amount of additional effort in collecting data on costs of compliance will be required. As we will explain, in a later section, there are limitations in quatifying nonmonetary costs, among which is the value of health and environmental damages.

We will be able to partially apply the model to some of the data on cost differentials from the case studies that we have conducted. Such a step is performed only for an illustrative purpose, since without further data it would be impossible to conclude whether the RCRA's regulatory requirements are optimal. Nevertheless, this excercise should show the operational feasibility of the model.

The Concept of Optimal Regulatory Requirements

Given the legislative objective of RCRA to prevent future improper disposal of hazardous wastes, the regulatory agency must choose a set of requirements that would be most effective in achieving this objective. We start by examining a firm's decision to comply with a certain standard required by regulation. In Figure I we have Firm A's marginal cost curve, C_a, for complying with a continuing level of standard, and a marginal cost curve, NC, for not complying with the required standard. With the horizontal axis representing an increasing level of standard, cost curve C_a slopes upward because we assume that it is more expensive to comply with the more stringent standards. The cost curve, NC, is constant. This assumes that regardless of what level of standard the firm incurs, fines, penalties and third party liability for noncompliance remain the same. However, it is possible that noncompliance penalties and fines or the probability of getting caught may change with new standards (e.g. the RCRA manifest system) so that NC becomes nonconstant. Since it is not our purpose to deal in-depth with the structure of noncompliance cost, we will merely point out that it consists of the expected value of loss from being caught and whatever cost is incurred during the illegal activity. The loss can be nonmonetary, such as corporate image and fear of imprisonment in the case of a criminal penalty.

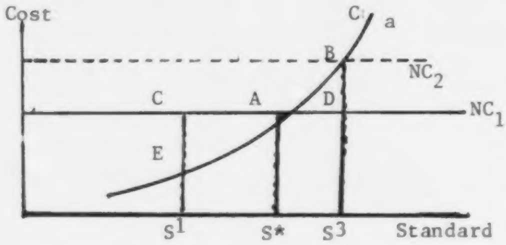


Figure I: Firm's Decision to Comply or Not

Whether Firm A will comply depends on whether the standard is to the left or right of point A, where the marginal noncompliance cost equals the marginal compliance cost. If the standard is set at S^1, firm A will certainly comply since the cost of noncompliance is greater than the cost of compliance by the amount CE. However, if the standard is set at S^3, the firm would rather not comply. Of course one can raise the cost of noncompliance to NC^2 so that S^3 becomes a compliance point. This occurs when penalties and fines of enforcement efforts are raised.

When industry has numerous producers with varying cost curves, the regulator faces the situation depicted in Figure II.

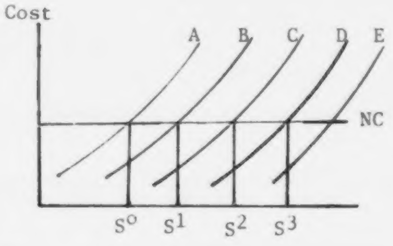


Figure II: Compliance Decisions on An Industry Level

There are five firms with Firm A and Firm E having the highest and lowest cost structures respectively for disposal of certain hazardous wastes. Let us say that before the promulgation of any regulation, all firms were handling waste in a manner equivalent to standard S^0. Assume a regulator imposes the standard S^1. When this occurs all of the firms, with the exception of Firm A, would comply and improve their disposal practice to S^1. The improvement in environmental quality due to Firms B, C, D, and E complying with standard S^1 is shown in Figure III.

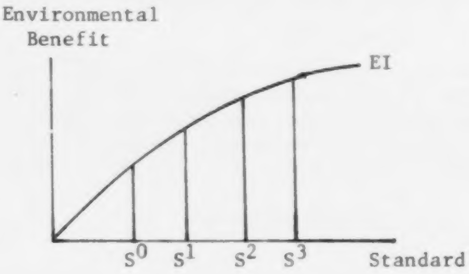


Figure III: Environmental Improvement Due to Additional Firms in compliance

If the regulator were to decide to push the standard to S^2, only firms C, D, and E would upgrade their practice and comply. Firm B, not only would not comply, but may go back to S^0 since it would not be in compliance anyway. This additional increase in the standard cause two effects: One is the additional improvement in the environment, as registered in Figure III, the other is a reduction in environmental quality due to Firm B dropping out of the compliance group and going back to its original level of waste handling practice indicated as S^0. This negative effect is registered by curve ED in Figure IV.

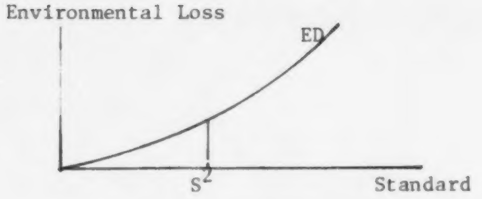


Figure IV: Environmental Degradation Due Firms Dropping out of Compliance

The shapes of EI and ED curves warrant some examination. The environmental improvement due to firms complying with the standards is shown by EI increasing at a decreasing rate. The underlying assumption is that as the standard becomes increasingly stringent, fewer firms will be willing to further improve their practices to be in compliance. This can be seen in Figure II as we move along the horizontal axis representing higher levels of standards. At the same time, the environmental degradation due to the firms dropping out of the compliance group increases because they are further away from the original level S^0. In other words, the opportunity cost of losing a firm to noncompliance is higher at a high level of standard. Thus the ED curve rises at an increasing rate in Figure IV.

The optimal standard (the one that results in the largest improvement in environmental quality) can be determined by combining the two curves, EI and ED, as shown in Figure V. At S^* the net environmental improvement is maximized. In an economic framework, when the marginal cost of raising the level of standard equals the marginal benefit of the move, the standard is at its optimal level. Maximum compliance is achieved through the cost minimization behavior of the industry.

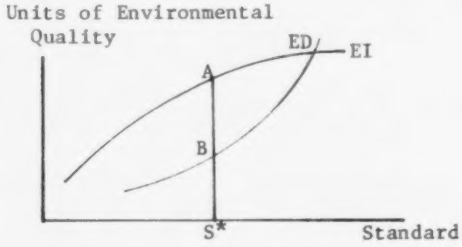


Figure V:Maximum Benefit from Optimal Std.

Compliance Model

It is not difficult to see that the cornerstone to the application of the above conceptual model is the ability to identify the marginal benefit and loss at each level of the standard. The benefit is derived from the firms that will remain in the compliance group and upgrade their practices. The loss comes from the firms that will drop out of the compliance group and return to their original improper practices. The link between the levels of standard and the entry and drop rates of the two groups are the cost differentials between compliance and noncompliance. The model to be presented primarily builds around the relationships between the marginal benefit and loss of the standards and the distribution of cost differentials across the firms that will be affected by the regulation.

Our compliance model can best be illustrated graphically. Figure VI presents a histogram showing the number of firms for each cost differential category for a given level of standard. The positive quadrant's horizontal axis represents how much more expensive it is to comply with the standards than not to. The negative quadrant's horizontal axis represents how much less expensive it is to comply with the standard than not to. Assuming that firms respond to cost advantage, the right quadrant contains the firms that would not comply and the left quadrant contains the firms that would. Figure VI is simply another way of presenting the information contained in Figure II, except it is for one standard at a time instead of one firm for each cost differential. We now have the number of firms for each cost differential categorgy. The latter change reduces the information requirement of the model.

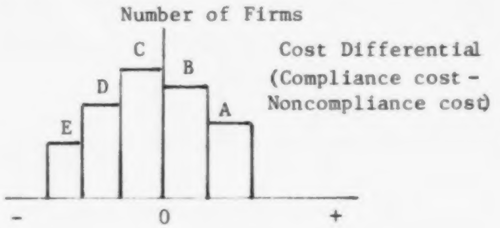


Figure VI: Cost Differential Distribution for Given Standard

The static situation in Figure VI can be made dynamic by introducing different levels of standard. Changing the standard would move the histogram along the horizontal axis. Standards increasing the cost of compliance will shift it to the right; ones decreasing the cost will shift it to the left. For example, the regulator can increase the stringency of the standard to the point at which category C enters the noncompliance group. This generalization is necessary since optimization of the standard must allow for variation in the level of standard. However, this is done through the employment of some assumptions. First, the ranking of the categories must be transitive: if A is greater than B and B is greater than C, A must be greater than C. Second, the ranking must be invariant as to the choice of the level of standard. These assumptions are not unreasonable, although the latter one may encounter trouble when the nature of the standard changes, allowing firms to trade places. For the model to operate we also need to be able to identify the relationship between the standards and the cost differentials. Such a relationship can be either derived from engineering data or estimated from several sample points. Given these assumptions we can assess the portion of industry under compliance.

Based on our conceptual model, as we incrementally tighten up the standard, there will be a marginal benefit and loss. Looking at Figure VI the question is, "what is the marginal benefit and loss when we shift the histogram so that one category of the firms will move into the noncompliance region?" We know some of the factors determining the marginal benefit and loss: the number of firms leaving the compliance region, the ones remaining in the region, the volume of waste generated by each category, and the level of standard where the firms drop out of compliance. We can even replace the assumption of constant marginal noncompliance cost with one of variable schedule based on firm size, since large firms tend to have a higher detection rate when they do not comply. Such factors can all be included into the model by assigning weights to the categories, as long as there exists a relationship between the factor and the cost differential. Looking at Figure VI it is obvious that the weighting factor is the number of firms. In other words, the assumption is that the number of firms in compliance or noncompliance is the policy variable with which we are concerned. Another choice is to weight the categories by the volume of waste handled. Or if it is considered important that firms with a large cost differential, due to their smallness in size, are more important the firms toward the right in Figure VI should be weighted heavier. Once the relevant factors are weighted, we can construct a net benefit index represented by the vertical axis in Figure VII.

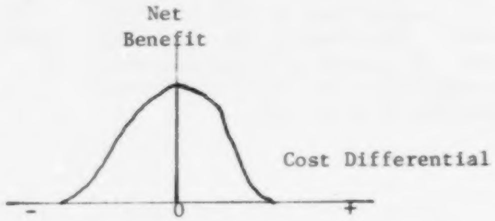


Figure VII
Distribution of Net Benefit by Cost Differential

The histogram is now turned into a smooth curve for the purpose of illustration. Now we can relate the cost differential back to the optimality condition. The areas under the curve are the net benefits of having the firms, based on their cost differentials, in the two regions. A standard should be chosen so that the vertical axis representing the breakeven point hits the top of the curve. At this point the standard is set so that its marginal loss, the slope of curve just to the right of the vertical axis, equals its marginal benefit, the slope just to the left of the axis.

Some comment on the shape of the curve in Figure VII is required, since the existence of optimality depends upon it. It was demonstrated earlier that without any weighting scheme, an optimal point exists because of the shapes of EI and ED in Figure V. Note that the vertical distance between the two curves corresponds to the curve in Figure VII. The question is whether weights based on other factors will change the curves so much that an optimal point can not exist. For example, what happens if the distribution of the numbers of the firms in each category produces two peaks, one at each end? It is then clear that two standards instead of one are necessary to maximize the net benefit. What if small firms are considered all important to be kept in compliance? Such a weighting will create a peak at the very end on the right-hand side of the curve so that as soon as a standard is increased from the minimum, the peak will intersect the vertical axis; further strengthening the standard will be undesirable. What if each category is valued equally? It is clear that no optimum exists since the curve will be a simple plateau. The result is again in accordance with the weighting scheme; without any ranking of the category one can set the standard anywhere. In summary, the resulting optimal standard always reflects the underlying assumptions considered to be important in setting of standards.

Limitations

It is clear that two types of difficulties will be encountered in utilizing the above compliance model. The first one is still the information requirements. These are: 1) the cost differential between legal and illegal disposal of the waste, and 2) the distribution of the cost differentials across the firms. In regards to the first type of information, one can obtain market values of wastes that are legally disposed of off-site, based on what the disposer charges. For the wastes that are disposed of on-site, the cost has to be constructed from the firm's engineering data.

The cost of illegal disposal is more difficult to obtain. It consists of several parts. One is the actual cost of illegally dumping the waste. This usually involves straightforward calculation of the cost of hauling the waste from the generator to the dumping site. In some cases, there may be little or no cost involved, e.g. disposing the waste in the existing landfill that does not comply with the RCRA standards. However, the major portion of the cost of illegal dumping comes from paying for the damages caused by the dumping when detected. This cost can be difficult to obtain, since assigning values to damages to health and the environment still faces various technical difficulties. Physical well-being and environmental goods are not traded on markets. Estimating the severity of the damage is also often impossible since scientific knowledge can not always establish the links between the exposure and final effects. However, since the decision to dispose of the waste legally concerns liability for damages rather than the true value of the damages, two factors can serve as bench marks. One of them is the financial ability of the illegal disposer to pay for the damage. Any assessment beyond the ability to pay will simply force the disposer to declare bankruptcy. When damages are likely to be high the disposer uses the net worth of his operation as the cost of noncompliance. The other factor is what the court assesses as damage. This means financial data of the firms involved with hazardous wastes management and past court decisions can be used to derive the cost differentials. Similarly, although the cleanup cost is difficult to estimate, its accuracy will not affect the cost differential once it is beyond the financial ability of the disposer. Finally, we have to consider fines and penalties. These costs, relatively small compared to the others, should be calculated at the maximum allowable by law. However, one complication may come from valuing corporate image and imprisonment. Firms realize that a negative image, such as one of social irresponsibility in dumping hazardous waste may lead to loss of business. It is also likely, since RCRA allows for criminal charges, that a corporate person would avoid possible jail sentences at a high cost. These intangible effects must be incorporated into the cost of noncompliance. A difficulty also arises when one has to translate these costs into expected value. This requires knowledge of perceived possibilities of detection and conviction. In other words, the disposer adjusts the cost of noncompliance by the possibility that he will be penalized and held responsible for the damages. For regulations that have been in effect for a while, some type of detection rate can be calculated from the enforcement record. The RCRA regulations, being relatively new, probably would not have such data. The researcher may have to assume several hypothetical detection rates and conduct a sensitivity analysis.

There are also difficulties in obtaining information on the distribution of the cost differential between compliance and noncompliance across the firms that are affected by the regulation. But this factor is crucial since determination of optimal regulatory standards can only be made at the industry level. For industries with few firms such data may be constructed from various existing industry profile data, or simply a survey of ongoing disposal techniques. For larger industries that generate and manage their own hazardous waste, an accurate account of the cost differentials may be impossible. An approximation has to be made through two steps. First, classes of representative firms have to be selected and their cost differentials calculated. Second, the distribution of these representative firms have to be assumed based on available data.

The second type of difficulty is to decide on the weighting scheme to be used for arriving at the net benefit. We admit that on technical grounds that more research is needed. However, on a conceptual level such practice can be defended. This is because it simply makes explicit the assumptions that regulators utilize. The weighting scheme also allows for sensitivity tests which enable the ultimate decision maker to form a range of alternatives, rather than accept or reject a single standard.

Construction of Costs Differentials[7]

As aforementioned, since we do not have the relevant data to apply to the compliance model completely, this section will only present the mechanics of calculating the cost differential between compliance based on past cases of illegal dumping. By analyzing the various types of cost in these cases, we can make some preliminary judgement as to whether firms of similar operation and size will comply to the existing RCRA regulations. The assumption underlying the judgement is that the cost of proper disposal that the illegal dumpers refused to incur represents the cost of complying with the existing RCRA regulations. The assumption is reasonable since the ultimate effect of the RCRA regulations is to induce proper disposal. The exercise in this section will end after cost differentials are calculated for the firms in the case studies. But theoretically the calculation can be repeated for firms of other sizes until enough categories can be created for subsequent analysis.

Each of the four case studies included for the cost differential analysis will be briefly summarized first. Different types of costs for the cases are calculated and put into. For illegal dumping or noncompliance we have the direct cost and expected cost. The former is the actual cost involved in illegally dumping the wastes. The latter is the expected cost resulting from the release being detected and the disposer found responsible. It consists of clean-up cost, fines and penalties and health and environmental damages. Although, the last item is listed in Table I, it is not quantified. Qualitative descriptions are made to the extent possible. The case studies also provided the direct cost of compliance or legal disposal of wastes. These costs are estimated by quoting what legitimate waste disposers would charge for disposing the wastes that was illegally dumped. These cases are:

A. Bullit County, Kentucky (Valley of the Drums)

The Valley of the Drums is located in a rural area in Bullitt County, Kentucky, fifteen miles south of Louisville. From 1967 through 1978 over 17,051 drums of chemical wastes were illegally stored on the ten-acre site. A number of drums were buried or emptied directly into pits. Soil and water samples taken by EPA have detected 197 organic chemicals and 28 metals, including 21 suspected carcinogens, mutagens, and teraogens and 26 priority water pollutants.

1. Direct and Expected Costs of Illegal Disposal

An estimate of the direct cost of illegal disposal or organic chemical wastes on the site is derived from the fee charged to industry to transport and dispose of the wastes and the total volume of wastes illegally dumped.

Taylor, the owner of the site, charged the industries involved 2.50 dollars per drum to transport and dispose of chemical wastes on his property. At the time of the sites closure in 1979, 17,051 drums of organic chemical wastes were present on the site. Combining these figures, the total direct cost of illegal chemical waste disposal on the site is 42,627 dollars.

The expected costs of illegally disposing of wastes on the site include the cost of cleaning up the property, the estimated cost of health and environmental da-

TABLE I

Costs of Legal and Illegal Dumping of Hazardous Wastes from Selected Cases

Illegal Dumping							Legal Dumping
				Expected Cost			
Case	Chemical	Volume	Direct Cost	Clean Up Cost	Health and Environment Damage	Fines and penalties (max)	Direct Cost
Bullitt County Kentucky	Organic Components	17,051 Drums	42,627	3,148,000	*	10,000	255,000-426,000
Chester Penn.	Hazardous materials	50,000	375,000	1,250,000-3,000,000	*	10,000	1,750,000-2,500,000
North Carolina	PCB	30,000 gallons	30,000	1,580,000	*	10,000	90,000-120,000
Dover N.J.	Organic Chemical	5,500 barrels	20,000	44,350	*	10,000	21,175-30,250

*Nonquantifiable

Source: ELI Case Studies

mages, and fines or penalties imposed on the owner of the property.

The total cost of cleaning up the site is expected to reach $3,148,000. U.S. EPA, Kentucky's Department of Natural Resources and private industry have provided the funding for clean up efforts thus far. EPA has contributed the largest share, with $328,000 spent for general clean-up operations and installing a recharge filtration system, and $200,000 spent for analysis of soil and water samples. In addition, the clean-up operations have cost EPA an undetermined amount in general administrative expenses.

The state of Kentucky has spent $24,391 in connection with the Valley of the Drums. The majority of this has been spent on arranging and supervising the clean-up efforts. In addition, the State expects to spend $10,000 to clean and recharge a filtration system on the site.

Five industrial firms who generated much of the waste dumped at the site have agreed to pick up and properly dispose of the wastes that they can identify as having originated with them. The five major generators of waste at the site expected to spend approximately $85,000 to remove 1,300 of the 17,051 drums present on the surface of the site.

Kentucky's state officals estimate that an additional $2.5 million will be required to completely analyze, remove, and properly dispose of the wastes dumped at the Valley of the Drums, bringing the total expected clean-up costs to $3,148, 000.

The expected health and environmental costs of the illegal disposal of chemical wastes at the site have not been quantified. Presumably, there has been a loss in the recreational value of Wilson Creek which abuts the site. The State of Kentucky has advised against fishing in the creek due to PCB contamination of fish.

Property damages have also not been quantified for the illegal disposal of chemical wastes on the site. However, the real property value of the land was assessed at $10,000 for County tax rolls in 1978. No one has been willing to purchase the property although the owner has been trying to sell the dump site. Therefore, the value of the property has, presumably, been decreased.

The third category of expected costs from the illegal disposal of chemical wastes on the site are fines or penalties envoked against the owner of the site. At the present time no such action has taken place. However, pursuant to the Comprehensive Environmental Response, Compensation, and Liability Act of 1980, (Superfund), an illegal disposer of hazardous wastes, as defined under Section 102 of the Act, shall upon conviction be fined not more than $10,000. The expected costs of fines or penalties against the owner of the site are therefore, quantified in this summary as the maximum allowable, or $10,000.

2. Direct Cost of Legal Dumping

Proper disposal of the wastes found at the Valley of the Drums would have cost between $15 and $25 per drum in 1976. The direct cost of properly disposing of the 17,051 drums of wastes present on the surfact of the site would have cost $255,000 in 1976 at the cost of $15 per drum and $426,000 at the cost of $25 per drum.

B. Chester Pennsylvania

Between 1974 and 1977 approximately 50,000 drums of chemical wastes were illegally stored and dumped on an industrial plant site along the Delaware River in Chester, Pennsylvania. The Pennsylvania Department of Natural Resources discovered the illegal site in 1977 and ordered it shut down. Two parties were involved in the illegal disposal: Wade, the owner of the site, and ABM disposal services, a waste transport company. In addition, Wade also profitted from an unidentifiable amount of drums to a near by waste recyclers.

1. Direct and Expected Lost of Illegal Disposal

The total direct cost of illegal disposal of hazardous wastes on the Chester Site is $375,000. This figure is derived from combining the amount ABM waste transport services paid wade, the owner of the site to accept the drums of waste and the $6.00 profit wade gained from emptying the drums of waste and selling the emptied drums to a recycler.

The expected losts from the illegal disposal include Clean-up costs, health and environmental damages, and the expected cost to the illegal disposer from fines or penalties.

Total Clean-up costs for the Chester Site are expected to range from $1,250,000 to $3,000,000. A breakdown of these costs includes $650,000 to remove drums from the site, and the remainder for clean-up of the Delaware River, removing the surface layer of soil from the site, and whatever measures may be needed to prevent the further spread of chemical contaminants.

Health and environmental damages have not been quantified for the Chester site. A substantial amount of heavy metals have contaminated the Delaware River and bottom sediment. U.S. EPA and the Pennsylvania Department of Natural Resoruces are currentlyinvestigating the amount of damage to the river and nearby groundwater services.

Property damages which have resulted primarily affect the value of the land where the wastes were illegally dumped. The owner has stated that the property was worth approximately $4,000,000, however, the most prospective buyers have offered for it is $750,000.

There have not been any penalties or fines assessed against the owner of the site. However, for purposes of this analysis we have used the $10,000 maximum allowable penalty for violation of Section 102 of (Superfund).

2. Direct Cost of Legal Disposal

Proper disposal of the hazardous wastes present in the Chester site would have cost approximately $35 to $50 per drum. This estimate is based on the average waste disposal charges of legally permitted disposal facilities located in the vicinity of the site. Combining these figures with the volume of waste illegally disposed at the site, the total cost of legal disposal of the wastes would have ranged from $1,700,000 to $2,500,000.

C. PCB in North Carolina

During a two mongh period in 1978 Robert Burns illegally disposed of approximately 30,000 gallons of transformer oil along 211 miles of rural foods in North Carolina. Federal regulations issued in the srping of 1978 permitted the disposal of PCB oils only in incinerators; since no inceneraters were operating in 1978 the oil could only be stored. However, Burnes contracted with Ward Transformer Company to illegally dispose of the waste, for this Ward received a kick-back from Burnes.

1. Direct and Expected Losts of Illegal Disposal

The total direct cost from the illegal disposal of PCBs is $30,000. This figure was derived from the amount paid to Burnes by Ward Transformer Company, the supplier of the PCB oil. Ward Transformer Company contracted with Burnes to dispose of the PCB oil at $1.70 per gallon. However, Burnes agreed to pay Ward 70¢ per gallon as a cash kick-back, making the actual cost of disposal $1.00 per gallon.

The expected costs from the illegal disposal of PCB's include clean-up costs, damages to health and the environment, and penalties or fines imposed against the illegal disposer.

Clean-up costs for the contaminated roadsides are expected to total at least $1,580,000. These costs include removing the contaminated soil from the road shoulders, reshaping the shoulders, hauling the contaminated material to the disposal site and constructing a proper disposal site.

The health and environmental damages from the PCB dumping have not been quantified. Agricultural produce was destroyed or not harvested as a result of the PCB spill but the extent of the loss was not monetized.

Charges have been brought against Ward and Barnes, however, no fines have been invoked. Burnes was sentenced to 3-5 years in prison, a trial on Federal charges against Burnes and Ward is slated for July 1981. The maximum allowable fine under Section 10s of the Act is $10,000. This figure has been used as the maximum expected fine in this summary.

2. Direct Cost of Legal Disposal

The total cost of the legal disposal of the PCB contaminated oil would have ranged from $3.00 - $4.00 in 1978. These figures are based on the charge per gallon for inceneration of hazardous chemicals at an approved facility owned by Rollins Environmental Services in Texas. The total cost of legal disposal may be derived from combining the charge per gallon by the volume of PCB contaminated oil that was discharged. At $3.00 per gallon the total charge for disposal would have been $90,000 and at $4.00 per gallon the cost of proper disposal would have been $120,000.

D. Dover, N.Y.

During an eight month period in 1971 a scavenger trucker under contract to Union Carbide Corproation disposed of between 5,000 and 6,000 barrels of chemical wastes on a former chicken farm in Dover Township, New Jersey. The wastes included aromatic hydrocarbons, benzene, tobrene, styrene, xylene, ketones, alcohols, and phenolic resins.

1. Direct and Expected Costs of Illegal Disposal

The direct losts of illegal disposal of hazardous wastes in Dover, New Jersey total $20,000. Union Carbide paid the scavenger trucker $3.50 per drum to haul away and dispose of approximately 5,500 drums of waste.

The expected costs of the illegal disposal of waste include clean-up costs, damages to health and the environment, and fines and penalties levied against the illegal disposer.

Clean-up operations on the site are expected to total $49,350. Dover Twonship has already spent an estimated $10,000 to inspect and supervise the removal of waste dumped at the Reich farm. Union Carbide has spent approximately $15,750 to remove 4,5000 drums from the site.

The health and environmental damages have not been quantified for the illegal disposal of wastes on the site. However, Union Carbide has given the owners of the property $10,000 and reimbursement for the cost of drilling a new well as compensation for damage done to their property as a result of dumping the waste. In addition 140 local residents have received $140,000 in total from Union Carbide as compensation for the loss of their wells. Both instances of compensation were initiated as a result of groundwater contamination from the illegal dump site. The State of New Jersey is also expected to receive up to $60,000 from Union Carbide in compensation for costs connected with any groundwater contamination that may occur after April of 1977.

The maximum fine or penalty allowed under Seciton 102 of Superfund is $10,000. This figure has been quantified as the maximum expected cost from fines or penalties in the illegal disposal of wastes on the site.

2. Direct Cost of Legal Disposal

The direct total cost of the legal disposal of the wastes would have ranged from $21,175 to $30,250. These figures are derived from the cost per drum of incineration of chemical wastes at a legal facility in New Jersey. Incineration would have cost $3.85 to $5.50 per drum, totalling $21,175 and $30,250 respectively for the 5,500 drums.

Cost Differentials with Varying Probability

The costs in Table I are transformed into cost differentials with varying probability of the disposer being held responsible for the release in Table II. The numbers with negative signs indicate it is still cheaper to comply than not to. Where the positive numbers indicate the cost of compliance has exceeded the cost of noncompliance, we can expect the incentive to dump illegally to be strong. In the case of the Valley of Drums in Bullit County, Kentucky, cost of noncompliance does not exceed that of compliance until the probability becomes.1. The same disposer would probably illegally dump again if the probability of detection is equal to .1 or less. The case of Chester, N.C. is clearly an example where costly regulation can prompt illegal dumping. Even at the certainty of 1.0 it is probably cheaper not to comply. On the other hand, both the case of North Carolina and the one of Dover, N.J. show tendency to comply even for small probability of being detected. The reason for the illegal dumping must have been either not knowing the consequence of the dumping or simply believing that one would not be caught.

The above results are subjected to a number of qualifications. First, as we have noted, health and environmental damages are not incorporated into the numbers presented in Table II. Of course, if these damages can be recovered, there will be an increase in incentive to comply. On the other hand, when the damages are in the area of millions of dollars, it is likely that the disposers do not have the financial profile of the disposers.

Summary

The qeustion of how to minimize illegal dumping or maximize compliance in the hazardous waste regulations is not only complex on the theoretical level, but also a difficult one to address on the empirical level. Although, economic theory can explain the mechanics of decision-making in compliance or noncompliance on a firm level, the extension of the theory to the compliance question on an industry level has been only occurred recently. Although the application of an industry compliance model still faces serious difficulties due to lack of relevant data, the recognition of the concept that overly burdensome regulations can be counterproductive is a noteworthy step foreward. (In time, relevant information may accumulate to produce adequate data base for the model.) Nevertheless, even if the information existed, it should be clear that the marginal benefit of regulation is often defined in the political arena; any result from a compliance model is based on a certain set of assumptions. Regulatory analysis should make them explicit as does the weighting scheme discussed in this paper. Such efforts should promote the regulatory efficiency much needed as our private industry is asked to bear more regulatory constraints.

Footnotes and References

1. Freeman, A. Myrick, Haveman, H. Robert and Kneese, V. Allen, The Economics of Environmental Policy, John Wiley & Sons, Inc. New York, 1973, p. 33.

2. For the difficulty in identifying social preference see Arrow, J. Kenneth "A Diffculty in the Concept of Social Welfare," Readings in Welfare Economis, Arrow,J. Kenneth and Scitousky, Tibor (Ed). Richard Iwrin, Inc., Illinois, 1969. Research in theory of economic surplus has dealt with the difficulty of calculating loss of social welfare due the misallocation of resources. See Currie, M. John; Murphy, A. John and Schmitz, Andrew "The Concept of Economic Analysis," The Economic Journal No. 324, Vol. LXXXI, Dec. 1971.

3. W. Viscusi and R. Zechauser, "Optimal Standards with Incomplete Enforcement," Public Policy, 27:437 (1979)

4. Illegal dumpins in this section includes any hazardous waste disposal, treatment and storage practice that causes improper release damaging to health and environment.

5. The distinction between environmental compliance model and environmental management model is that the former model operates for any given level of environmental quality. Unlike the latter, it does not determine the socially optimal level of envrionmental quality. In other words, once the optimal level of environmental quality is determined through some process, be it political, economic or legislative, the compliance model decides the most efficient level of standard to achieve this specified level.

6. For example, see Becker, Gary, "Crime and Punishment: An Economic Approach," in G. Becker and W. Landes (EDs.) Essayse in the Economics of Crime and Punishement, Columbia University Press, New York, 1974, pp. 1-54.

7. We have suppressed the footnotes identifying the source of the cost estimation due to their number.

TABLE II

Differentials in Cost Between Legal and Illegal Disposal of Hazardous Wastes[1]

Bullit County		Chester		North Carolina		Dover	
P.[2]	CF[3]	P	CF	P	CF	P	CF
1.0	-2,860,000	1.0	177,500	1.0	-1,515,000	1.0	-53,600
.5	-1,232,000	.5	963,750	.5	- 720,000	.5	-24,000
.3	- 603,000	.3	1,273,250	.3	- 402,000	.3	-12,000
.1	26,220	.1	1,592,750	.1	- 84,000	.1	- 200

[1] Cost differentials are calculated from Table I. When there is a range, the mean is used.

[2] Probability of detection and conviction

[3] Cost Differential

Source: ELI Case Studies

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/9-81-002b	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Land Disposal: Hazardous Waste Proceedings of the Seventh Annual Research Symposium		5. REPORT DATE March 1981 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Edited by David Shultz Coordinated by David Black		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Southwest Research Institute P. O. Drawer 28510 San Antonio, TX 78284		10. PROGRAM ELEMENT NO. BRD1A DU109 11. CONTRACT/GRANT NO. 68-03-2962
12. SPONSORING AGENCY NAME AND ADDRESS Municipal Environmental Research Laboratory--Cin.,OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268		13. TYPE OF REPORT AND PERIOD COVERED Final - 9/20-3/81 14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES
Project Officer Robert E. Landreth, 684-7871

16. ABSTRACT

The Seventh Annual SHWRD Research Symposium on land disposal of municipal solid waste and industrial solid waste and resource recovery of municipal solid waste was held in Philadelphia, Pennsylvania, on March 16, 17, and 18, 1981. The purposs of the symposium were (1) to provide a forum for a state-of-the-art review and discussion of on-going and recently completed research projects dealing with the management of solid and industrial wastes; (2) to bring together people concerned with municipal solid waste management who can benefit from an exchange of ideas and information; and (3) to provide an arena for the peer review of SHWRD's overall research program. These proceedings are a compilation of papers presented by the symposium speakers. The technical areas covered in the Land Disposal: Municipal Solid Waste are gas and leachate production, treatment and control technologies and economics. The areas covered in Land Disposal: Hazardous Wastes are hazardous waste characterization, transport and fate of pollutants, hazardous waste containment, land treatment of hazardous wastes, hazardous waste treatment, uncontrolled sites/remedial action, and economics. Municipal Solid Waste: Resource Recovery include the areas of equipment and processing, recovery and use of materials, environmental aspects and economics/impediments and special studies.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Leaching Collection, Hazardous Materials, Disposal, Treatment, Soils, Groundwater Pollution, Waste Treatment, Methane, Gases, Linings	Solid Waste Management Sanitary Landfills Hazardous Waste Leachate	13B

18. DISTRIBUTION STATEMENT Release to public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

☆ U.S. GOVERNMENT PRINTING OFFICE: 1981-757-064/0244